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THE Journal OF THE AMERICAN LEATHER CHEMISTS ASSOCIATION

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The Journal
of the
AMERICAN LEATHER CHEMISTS ASSOCIATION

Vol. LV NOVEMBER 1960 No. 11

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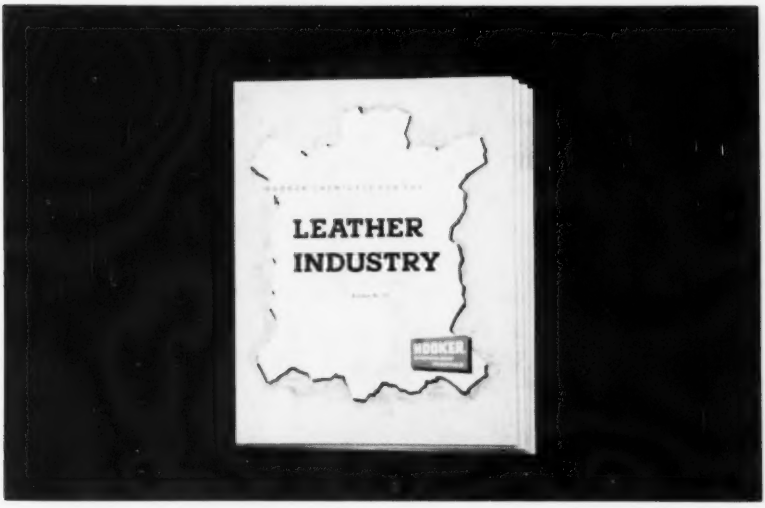

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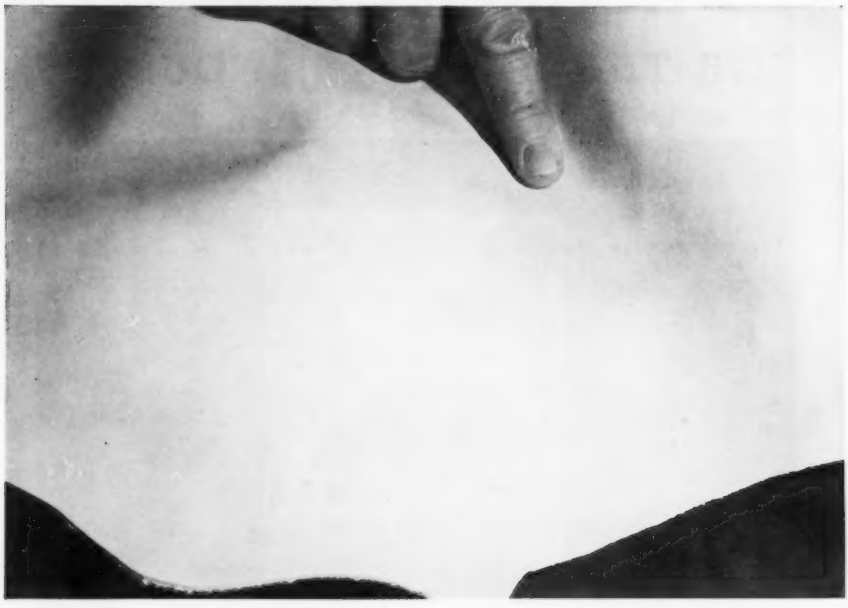

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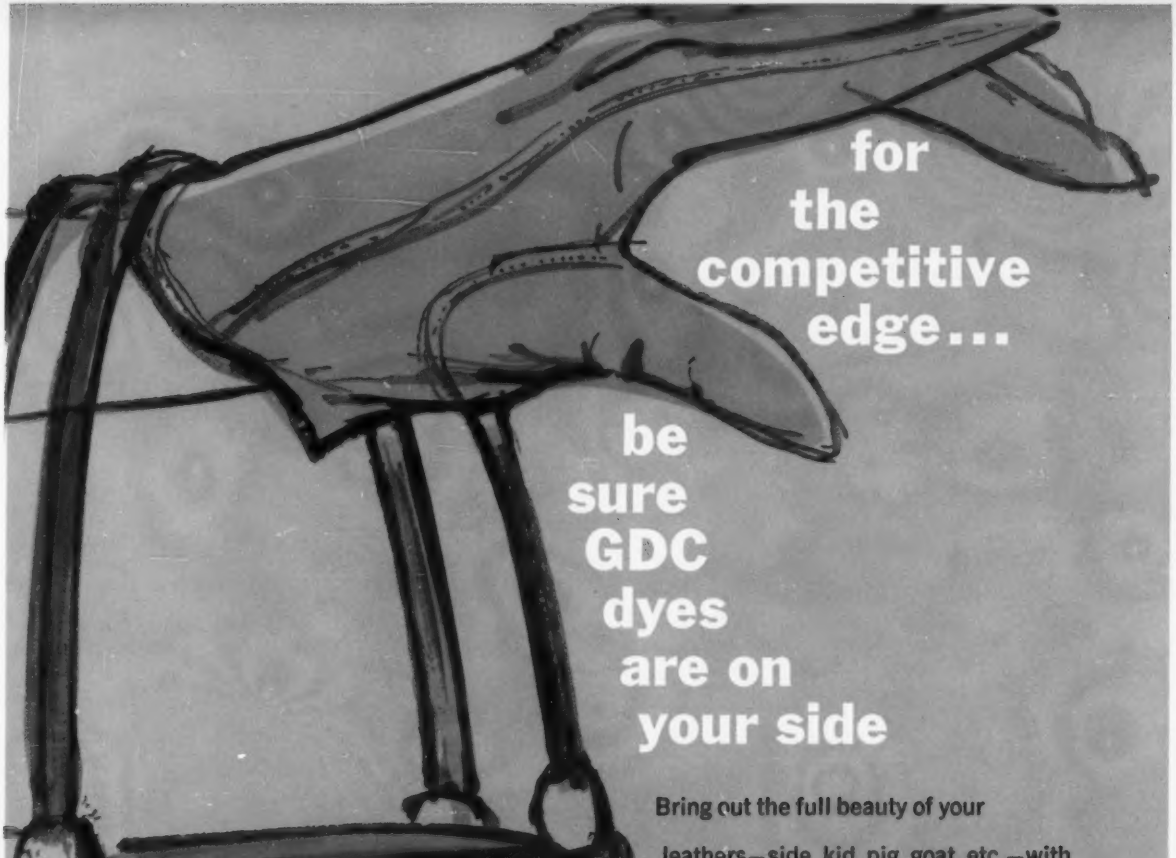
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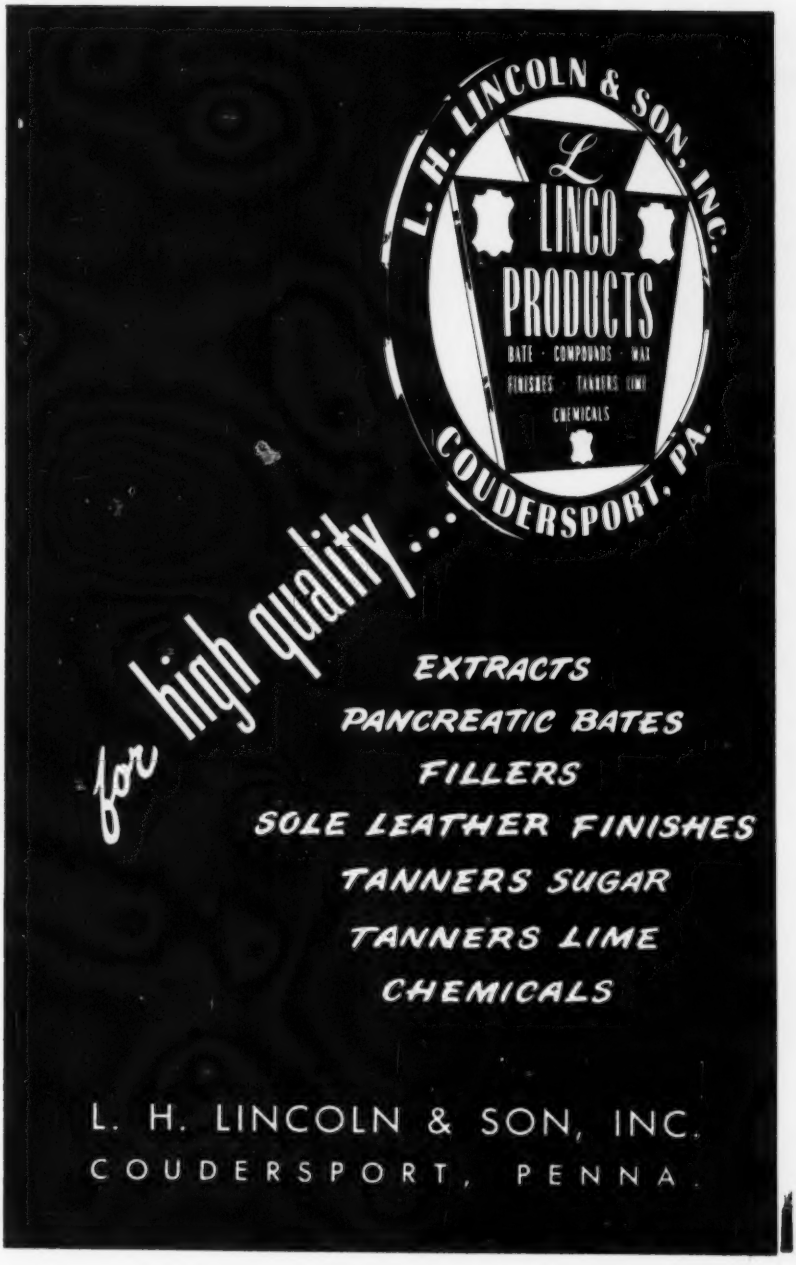
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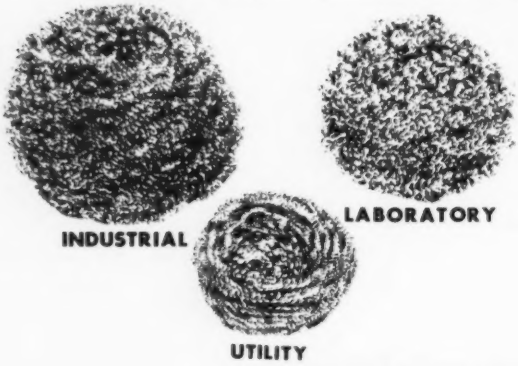

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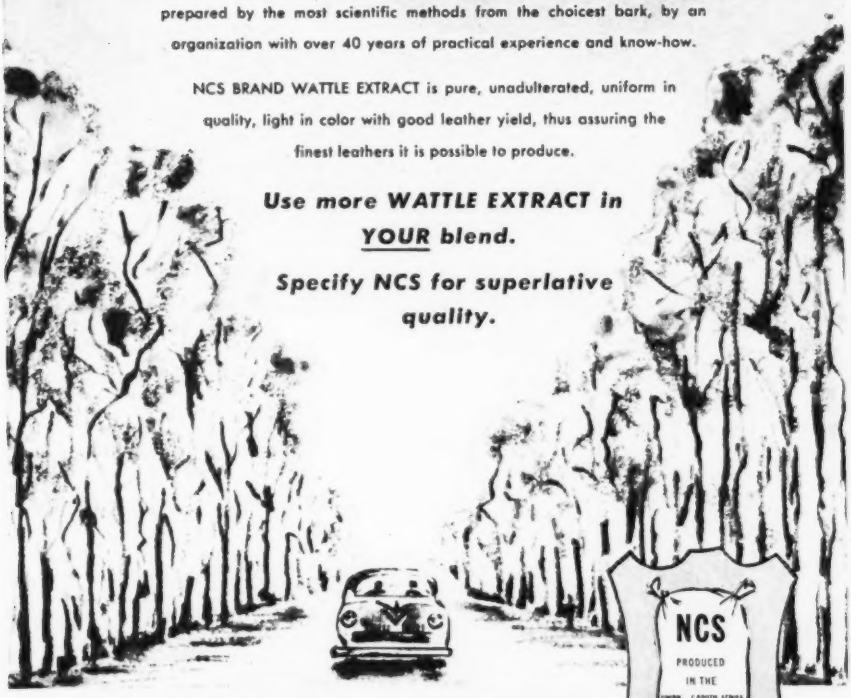

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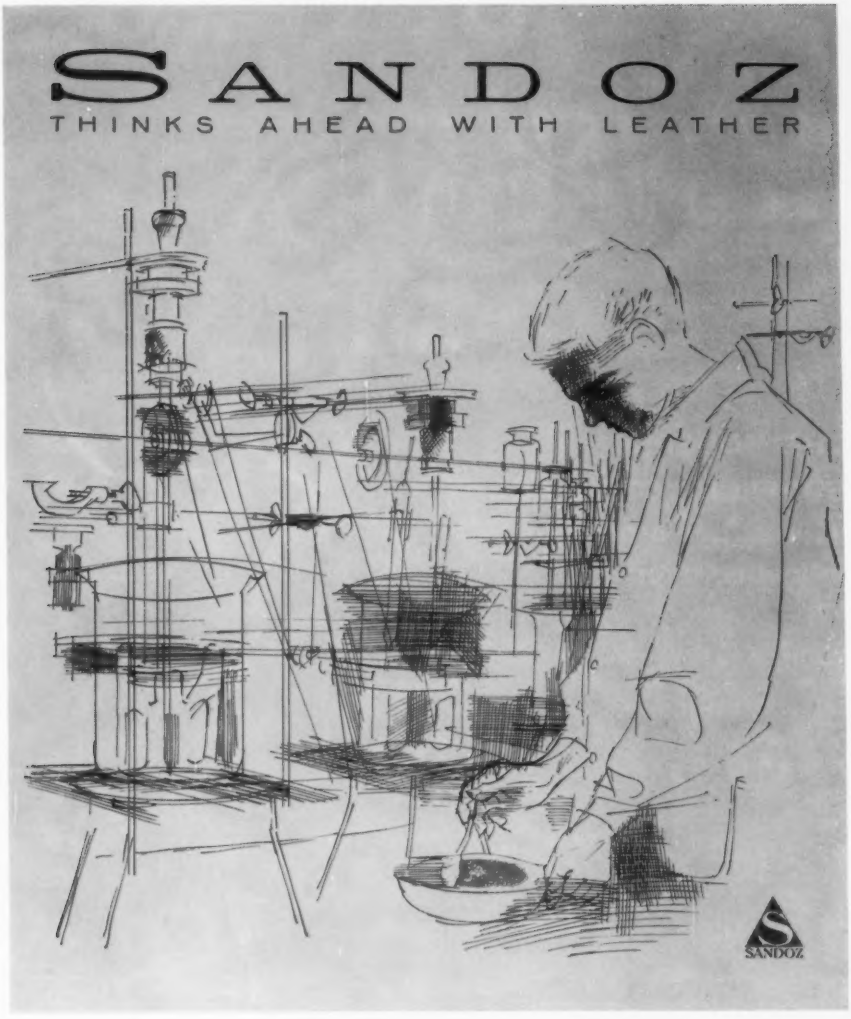

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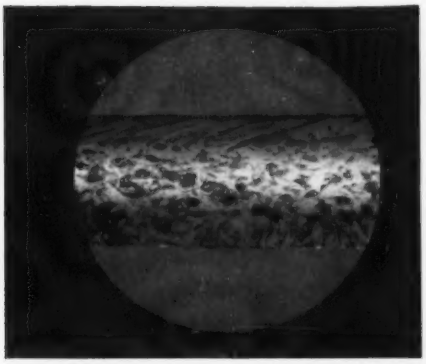

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STUDY OF THE EFFECT OF THE ELASTIC TISSUE OF HIDE ON THE PHYSICAL PROPERTIES OF LEATHER*

CONRAD L. ORNES AND WILLIAM T. RODDY

Tanners' Council Laboratory
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and

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Philadelphia 18, Pennsylvania

ABSTRACT

This paper is a report of the results of over two years of laboratory and plant work in developing a method for removing elastic tissue from cowhide under controlled conditions and in studying the effects of such removal on the physical properties of the leather produced. The evidence is conclusive that removal of elastic tissue from cowhides by means of Viokase enzyme causes the leather produced from such stock to have softer temper, coarser break, and more drawn grain than the corresponding control leather. Physical tests indicate that the removal of elastic tissue from cowhide stock caused the leather produced from such stock to have higher tensile strength and higher stitch tear strength as well as a more flexible grain.

INTRODUCTION

Much of the present knowledge about elastic tissue has been summarized by Highberger (1), who states that elastic tissue appears in most connective tissues of the body, is yellow in color in the native condition, and is found in close association with collagen. Small quantities of elastic tissue are present in the skin, mostly in the grain and the flesh layer, where the tissue exhibits a characteristic branching form, and in the arterial system. Elastic

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**A laboratory of the Eastern Utilization Research and Development Division, Agricultural Research Service, United States Department of Agriculture.

tissue is extremely resistant to water and can be boiled with no apparent effect. It is much more resistant than collagen to acids, alkalies, and some enzymes.

In determining the properties of elastic tissue, most of the work has been done on elastin-rich material such as the neck ligaments of cattle and large arteries. It is comparatively easy to purify the elastic tissue in these materials by extracting everything else, leaving the purified elastic tissue as a residue. Interest in removal of elastic tissue in skin without damage to the associated collagen probably received its greatest impetus from the work of Roddy and O'Flaherty (2) who showed that the elastic tissue in calfskin is not appreciably affected by any of the pre-tanning operations but becomes hard and brittle after tanning and drying.

Following this work, Pleass (3) concluded from a microscopic study of finished glove leather that, although elastic tissue is present in a broken-down state, it has no correlation with the degree of run of glove leather. White and Caughley (4) concluded that elastic tissue fibers do not perform an important part in the tightness of grain during the wet process but may play an important role in the tightness of dry leather. The present work is the first attempt to correlate the physical properties of finished leather with the removal of definite amounts of elastic tissue.

In work done at the Eastern Utilization Research Laboratory of the Department of Agriculture, Hoover *et. al* (5) have been able to isolate the grain layer of bovine skin and have found it to have properties very close to those of elastic tissue. Mellon and Korn (6) at the same laboratory demonstrated by means of horizontal sectioning and chemical fractionation that this condensed grain membrane was the result of the collapse of the 3-dimensional network of elastic tissue fibers as usually seen in the microscopic examination of stained cross sections of skin. The problem at hand then becomes one of measuring by chemical or physical means any changes in the amount of the elastic tissue and relating such changes to the physical properties of the leather produced from such modified skins.

Almost forty years ago Wilson (7) advanced the idea that the chief function of the enzyme in the bate was the removal of elastic tissue. He and co-workers were able to demonstrate by means of cross sections of calfskins before and after bating that the removal of elastic tissue was a function of concentration of enzyme and time. However, Hollander (8) showed by histological study of bated skins that the elastin fibers are not completely removed by bating action. More recently the dissolution of elastic tissue by the enzyme elastase has been studied by Balo and Banga (9) and by Hall and Gardiner (10). They used elastic tissue which they prepared from aorta and ox ligamentum nuchae. They found that elastic tissue from these sources could be dissolved by elastase derived from pancreatic extract. More than 70 per cent of their elastic tissue preparations was dissolved. Hoover, *et*

al. (5) found that the grain membrane which they identified as elastic tissue could be dissolved by trypsin. In the present work the elastic tissue was removed from skin and hide by use of a pancreatic product.* The elastase activity of this product, when measured by the formol titration method of Cordon *et al.* (11) at a concentration of 167 mg. of enzyme per 100 ml. of solution at pH 8.5, was 7.64 meq. of nitrogen liberated per gram of enzyme. The protease (PV) activity measured by the Gross-Fuld method (12) was 81,500 PV units per gram of enzyme at pH 7.0.

EXPERIMENTAL PROCEDURE

General Considerations

Limed hide, ready for bating, contains essentially water, lime, lipids, collagen, hair-root debris, some globular protein, and elastic tissue. The development of a method of measuring the amount of elastic tissue in limed hide then involves purifying the relatively inert elastic tissue by removing the associated components. Only the hair-root debris offers any serious difficulty in the process of purification, since the other components are soluble in water, acid, and fat solvent. Tancous (13) has shown that the elastic tissue-keratin residue amounts to only 2.4 per cent of the total protein on a nitrogen basis in pickled calfskin. The nitrogen basis was also used by Hoover, *et al.* (5) in determining the amount of the grain membrane previously cited, which also contained hair-root debris. Stubbings (14) also used the nitrogen basis in his calculations in his attempt to separate the elastic tissue and hair-root fractions by means of treatment with sodium sulfide.

Since the interest of the present investigation is in the measurement of the loss of elastic tissue from the hide, the presence of hair-root debris in the purified residue becomes unimportant if its distribution in the hide under test can be shown to be uniform. Such considerations led to the use of the dry weight of the purified elastic tissue-keratin residue, expressed as a per cent of the dry weight of the limed or bated hide, as a basis for calculating the loss of elastic tissue due to enzymatic action.

Purification of Elastic Tissue-Keratin Residue

The use of the autoclave (6) enables one to dissolve the collagen from the limed hide in a reasonable length of time without affecting the elastic tissue. Time-rate studies using the hydroxyproline assay to determine when all of the collagen had been removed from the residue were used to establish the minimum time required. The resulting grain membrane in a solution of

*The product, called Viokase, was a commercial preparation from a whole raw pancreas which had been activated, desiccated, and defatted. This product was manufactured by the Viobin Corporation, Monticello, Illinois. The mention of trade names or companies does not constitute an endorsement of the Department of Agriculture over other products of a similar nature not mentioned.

gelatin was then filtered while hot and washed free of soluble proteins and lime by alternate washes with hot water and hot dilute acid. Lipids were then removed by extracting with acetone. The detailed method is as follows:

1. Press representative squares of limed hide or skin, approximately 1½" in size, individually in a Carver press at 10,000 pounds ram pressure to remove most of the water.

2. Dry the squares in a vacuum oven at 22" of mercury and at 80° C. overnight to furnish a dry-weight basis.

3. Add sufficient distilled water to make a 2-3 per cent gelatin solution assuming all of the dry weight is collagen. Autoclave at 15 pounds pressure for four hours.

4. Filter while hot through tared, coarse-fritted glass crucibles and wash free from lime and soluble proteins using alternate washes of hot water and hot 0.5*N* HCl. Finally wash free of acid with hot water. Suction may be used but in some cases may cause the filter to clog.

5. Place the crucibles in Soxhlet apparatus, and extract with acetone for four hours.

6. Air-dry to remove acetone, and finally dry in a desiccator to constant weight. An overnight period is satisfactory.

Laboratory Tests to Remove Elastic Tissue

A side of heavy cowhide was obtained from a tanner of side upper leather. This side had gone through the regular soaking and beamhouse operations including unhairing and fleshing. It was received in a wet condition, wrapped in a plastic bag. The side was large enough to permit marking the pattern of specimens shown in Figure 1. After numerous preliminary tests the following procedure was used on the test specimens:

1. Place 10 specimens in a jar with water volume equal to 3 to 1.

2. Surface delime with 0.75 per cent HCl for ½ hour at 75° - 77° F. The end pH of the liquid should be neutral to methyl orange.

3. Add 2.25 per cent boric acid, and run for one hour.

4. Let stand overnight to delime completely.

5. Start heating, and add 1.5 per cent borax. Run for ½ hour. The pH should be 8.5 to 9.0 and the temperature 90° F.

6. Add pancreatic product, and treat for the required time at 90° F.

7. Remove the specimens, blot on towels, wrap in groups of ten, and store in the freezer until needed. Then proceed as previously described under purification of elastic tissue-keratin residue.

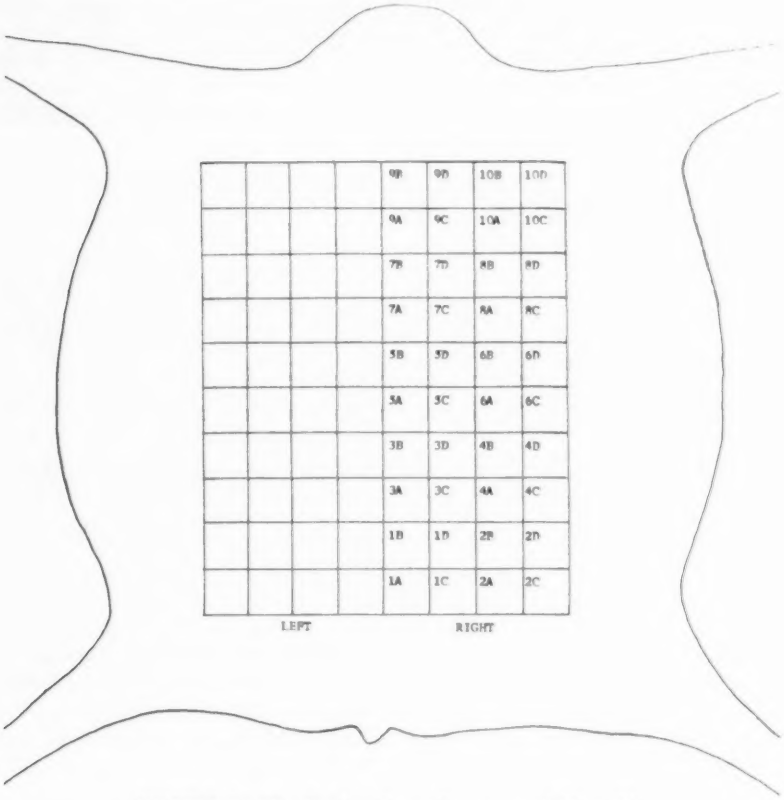

FIGURE 1.—Distribution of sample squares within a skin.

Pilot-Plant Test for Removal of Elastic Tissue

In the pilot-plant test 60 matched sides were used. Thirty sides (even lefts and odd rights) were selected from the 60 matched sides for three elastic tissue removal experiments as follows:

Lot A-7 0.05 per cent pancreatic product, 10 sides.
Lot A-8 0.10 per cent pancreatic product, 10 sides.
Lot A-9 0.20 per cent pancreatic product, 10 sides.

The 30 sides which matched the above 30 experimental sides were used as controls. Three pairs of matched sides were used to compare regular production wash and bate procedure with special deliming procedure used on all of the above 60 sides.

Treatment of lot A-7—Even left and odd right sides numbered 1-10 weighing 250 pounds were treated as follows:

1. Floated and washed 5 minutes at 75° F.
2. Drained.
3. Floated at 300 per cent (90 gals.) at 75° F.
4. Added 0.75 per cent (1 pound, 14 oz.) HCl in 3 gals. water at 75° F. and ran 30 minutes at pH of liquor 6.0 to 6.5. (This procedure was used to clear the grain surface of stains.)
5. Added 2.25 per cent (5 pound, 10 oz.) boric acid and ran one hour. pH of liquor 7.2.
6. Rested overnight to delime. pH of liquor 8.0.
7. Removed stock and heated liquor with live steam to 97° F., turned the drum and added stock, turned the drum again, at 93° F. 1.25 per cent borax was added with stock. pH of liquor 8.5 to 9.0.
8. Added 0.05 per cent pancreatic product (2 oz.). Ran 2 hours. pH of liquor 8.5 to 9.0.
9. Drained and floated and washed 10 minutes at 75° F.
10. Transferred to production drum with controls for pickle and chrome tan.

Treatment of lot A-8—Even left and odd right sides numbered 11-20 weighing 248 pounds were run the same as Lot A-7 except for the use of 0.10 per cent pancreatic product in step No. 8.

Treatment of lot A-9—Even left and odd right sides numbered 21-30 weighing 250 pounds were run the same as Lot A-7 except for the use of 0.20 per cent pancreatic product in step No. 8 and a run of 4 hours instead of 2 hours. Note: Three lefts, numbers 31, 32, and 33, were bated, pickled, and chrome-tanned with regular production and put with experimental and control sides for succeeding operations.

Treatment of controls to lots A-7, A-8, A-9—Odd lefts and even right sides numbered 1-30 and right sides 31-33 weighing 847 pounds were handled the same as Test Lots A-7, A-8, and A-9 up to step No. 8. At step No. 8 they

were bated with 0.75 per cent Oropon FS and run 45 minutes at 92° F. Steps 9 and 10 were the same as the treatments for test lots A-7, A-8, and A-9.

The experimental and control sides were then pickled and chrome-tanned using the regular production procedure. When the chrome had completely penetrated the stock, the chrome was set with sodium bicarbonate at pH 3.40 using 0.7 per cent sodium bicarbonate instead of the regular 0.5 per cent because less acid was neutralized by the completely delimed stock. The shrinkage temperature of the stock was 212° F. after the chrome was set. The stock was fatliquored and finished as a brown pigmented finished leather.

In the crusted state and as finished leather the stock was examined by experienced sorters for evaluation of the stock. The finished leather was shipped to the laboratory where analyses and physical tests were conducted to determine what influence the removal of the elastic tissue had on the finished leather. The results obtained and a discussion of the results are given in the following section.

RESULTS AND DISCUSSION

In Table I the results of the laboratory tests for removing elastic tissue from cowhide are given. The elastic tissue-keratin residue was reduced sufficiently in each case to indicate that plant tests should produce leather with variable amounts of elastic tissue. The thickness of the stock was found to have an appreciable effect on the efficiency of removal.

Three sets of ten sides each, representing the three levels of pancreatic product concentration, were compared with their alternate sides as controls. In the physical tests the differences between pairs were used to interpret the significance of the effects of the enzyme. In some cases only the average values are given in the tables in order to reduce the voluminous data. Averages were then compared on the basis of between- and within-skin variances. The usual "*t*" test data are also available for comparison of any two groups.

Table II shows the per cent decrease in elastic tissue for each side. It is obvious that much greater efficiency of removal of elastic tissue was produced in the plant test compared with the previous laboratory work. This may be attributed to the greater "mill" action obtained in the plant which literally pumped the reacting solution through the hides. In any case there is no doubt that most of the elastic tissue has been removed from the test sides. This was also verified by a study of stained cross sections. At the .05 per cent level of pancreatic product in the plant runs, this concentration removed 64 per cent of the elastic tissue from the cowhide over that obtained with the regular bating procedure.

TABLE I

PER CENT ELASTIC TISSUE RESIDUE REMAINING IN MATURE COWHIDE AFTER TREATMENT WITH A PANCREATIC PRODUCT

Location of block in the skin	Per Cent Pancreatic Product			
	0% (control)	0.03% (2 hours) No. 1	0.10% (2 hours) No. 2	0.20% (4 hours) No. 3
A	1.31	0.90	0.66	0.31
B	2.16	1.99	0.68	0.61
E	0.98	0.92	0.49	0.29
G	1.24	1.43	0.89	0.31
H	1.28	1.17	0.63	0.23
J	1.75	2.33	0.97	0.59
K	1.05	0.88	0.69	0.30
L	1.92	1.20	0.68	0.45
M	0.93	0.80	0.69	0.24
N	1.24	1.06	0.72	0.38
O	1.24	0.91	0.46	0.30
P	1.34	1.08	0.82	0.38
R	1.16	1.50	0.70	0.37
S	1.20	1.05	0.88	0.40
T	1.16	1.02	0.76	0.33
U	1.20	1.39	1.01	0.48
W	0.99	0.92	0.44	0.34
X	1.22	1.03	0.90	0.39
Y	0.88	0.66	0.41	0.18
Z	1.98	0.97	0.91	0.28
Average	1.31	1.14	0.72	0.36
Standard Deviation	0.36	0.40	0.18	0.11
Per cent decrease in residue		13.0%	45.0%	72.7%

Tables III and IV show the results of the laboratory evaluation of crust and finished side leather. Methods (15) have been developed at this laboratory for the measurement of such practical values as temper, mellowness, and break. These laboratory measurements have been reported to correlate with plant evaluations of the same properties. No significant effect of enzyme action on temper is shown in any of the two tables, although there is a trend toward more firmness for control leathers. The measurement for mellowness shows inconsistency of significance but in no case shows more than 4 per cent difference between averages and would therefore indicate no practical effect of pancreatic product treatment. In the measurement of break, which shows

TABLE II

PER CENT DECREASE IN ELASTIC TISSUE RESIDUE AFTER TREATMENT WITH A PANCREATIC PRODUCT

Side Leather Stock

Side No.	Low Level 0.05% (2 hours)	Side No.	Medium Level 0.10% (2 hours)	Side No.	High Level 0.20% (4 hours)
1	74.1	11	75.2	21	81.5
2	26.6	12	82.6	22	85.5
3	62.7	13	75.3	23	79.1
4	75.1	14	91.3	24	83.6
5	70.1	15	77.3	25	89.6
6	58.9	16	86.8	26	80.1
7	43.4	17	76.4	27	84.0
8	69.2	18	90.1	28	76.3
9	74.6	19	86.0	29	83.3
10	82.5	20	80.1	30	77.8
Average	63.7		82.1		82.1

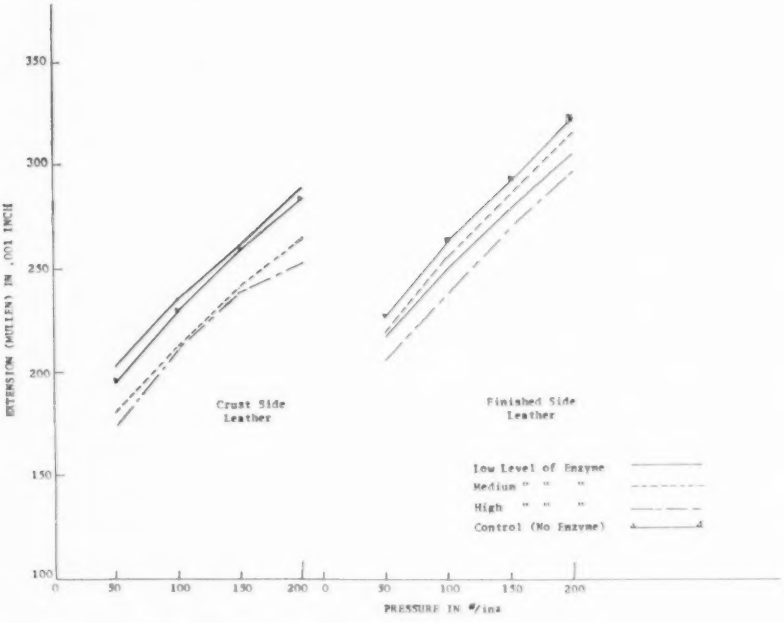

FIGURE 2.—Average Mullen stress-strain values.

TABLE III

LABORATORY EVALUATION OF EFFECT OF ELASTIN REMOVAL ON THE PHYSICAL PROPERTIES OF LEATHER

Crust Side Leather
(Average values)

	Low Level of Pancreatic Product (0.05%)		Medium Level of Pancreatic Product (0.10%)		High Level of Pancreatic Product (0.20%)	
	Test	Control	Test	Control	Test	Control
Temper Values (Compressometer)	39.8	41.0	36.2	38.0	41.9	43.8
Mellowness (Hardness Gauge)	81.8	80.8	80.8*	82.8	80.5	79.3
Break (Hopton Machine)	21.5	20.0	19.4	19.4	19.5*	23.0
Stitch Tear Lbs./in.	1167*	1017	884	877	997	964
Mullen Tests Pressure at Grain Crack	502	424	392	346	492*	332
Permanent Set (in .0001")	186	180	156*	184	146	153
Extension at 200 lbs. Pressure (in .001")	289	284	266*	297	254	272
Tensile Tests (Full Thickness) Lbs./in.²	3766*	3141	2758*	2397	3473*	2650
Per Cent Extension at Break	32.8	37.0	29.5	26.4	31.6	30.3
Pounds Pull at 1st Cycle	89.1*	73.4	76.3	70.3	82.8	76.1
Tensile Tests (Grain Only) Lbs./in.²	2940*	2505	2946*	2543	2862	2712
Per Cent Extension at Break	20.6*	18.0	21.4	19.1	21.3	19.8
Pounds Pull at 1st Cycle	13.1*	14.9	11.9	15.9	13.7*	16.8
Tensile Tests (Corium Only) Lbs./in.²	3375	2868	2390	2094	2636	2462
Per Cent Extension at Break	38.7	39.0	37.8	36.4	34.4	39.4
Pounds Pull at 1st Cycle	56.2	49.9	40.2	35.1	50.6*	43.1

*Indicates Statistical Significance.

TABLE IV

LABORATORY EVALUATION OF EFFECT OF ELASTIN REMOVAL ON THE PHYSICAL PROPERTIES OF LEATHER

Finished Side Leather
(Average values)

	Low Level of Pancreatic Product (0.05%)		Medium Level of Pancreatic Product (0.10%)		High Level of Pancreatic Product (0.20%)	
	Test	Control	Test	Control	Test	Control
Temper Values (Compressometer)	26.0	28.0	27.0	25.0	29.3	30.0
Mellowness (Hardness Gauge)	78.3*	76.3	77.2	77.1	83.0*	80.0
Break (Hopton Machine)	56.0	58.8	53.1	56.2	51.3*	63.2
Stitch Tear Lbs./in.	1232*	1114	1062*	928	1108	1082
Mullen Tests Pressure at Grain Crack	522	467	455*	385	563*	445
Permanent Set (in .001")	165	168	160*	175	149*	166
Extension at 200 lbs. Pressure (in. .001")	307	316	315	329	297*	322
Tensile Tests (Full Thickness) Lbs./in.^{2}	3278	3181	2928*	2614	3376*	2903
Per Cent Extension at Break	47.1	46.5	44.4	44.8	43.3	45.9
Pounds Pull at 1st Cycle	57.7	56.8	55.2	49.8	62.3*	52.7
Tensile Tests (Grain Only) Lbs./in.^{2}	1929	1962	2166	1954	2078	1857
Per Cent Extension at Break	33.2	30.6	29.2	27.6	30.6	28.1
Pounds Pull at 1st Cycle	13.5	17.3	16.9	18.4	16.0	17.3
Tensile Tests (Corium Only) Lbs./in.^{2}	2821	2825	2046	1860	2285	1912
Per Cent Extension at Break	43.0	48.5	39.6	40.7	35.9	39.5
Pounds Pull at 1st Cycle	38.7	33.6	30.6	26.3	35.8	27.3

*Indicates Statistical Significance.

the average width of the wrinkles produced by flexing, finer break is indicated by lower values. Here again the results are inconsistent for crust side leather but show a tendency for finer break for the test leathers of finished side leather. The average stitch tear strength of pancreatic product treated side leather is consistently higher than that of the controls but not always at a significant level.

Stress-strain studies were made of all the leathers in two different ways, and the results are shown in Tables III and IV, as well as in Figures 2, 3, and 4. The Mullen Tester was used in one study to obtain the vertical extension of the leather sample while it was held between the clamps and hydraulic pressure was applied to the flesh side. The vertical extensions at 50 pounds, 100 pounds, 150 pounds, and 200 pounds pressure were noted as shown in Figure 2. The pressure was then released, and the extension remaining after one minute of rest was recorded as the permanent set. Pressure was then applied again to determine the pressure required to crack the grain. As shown in Figure 2 no appreciable effect of enzyme treatment and no consistency was shown for any of the leathers. It is interesting to note that none of the curves cross. The pressure at grain crack as shown in the tables is consistently higher for test leathers. The permanent set in most cases is lower for pancreatic product-treated cowhide leathers. The extension at 200 pounds pressure is generally less for the pancreatic product-treated cowhide leathers although not always to a significant degree.

The Instron machine was used to study the stress-strain characteristics of dumbbell samples of $\frac{1}{2}''$ width. Two cycles were used. In the first cycle the jaws pulled the sample at the rate of 10″ per minute to extend it 25 per cent, and then it was returned to the starting position. After one minute of rest the sample was broken on the second cycle using the same jaw speed. The force being exerted on the specimen at all times was recorded automatically on the chart of the machine, and the stress-strain values shown in Tables III and IV and Figures 3 and 4 were obtained from these data. Since most of the elastic tissue of hide is concentrated in the grain, it was considered advisable to study the stress-strain characteristic of the grain and corium separately in addition to the study made of the full thickness.

If we consider the low, medium and high levels of pancreatic product treatment in Figure 3, curves of all three of the full-thickness enzyme-treated leather groups show that more force is required to extend leather from which the elastic tissue has been removed. This agrees also with the results of the Mullen test. The tensile strength of all the full-thickness leathers is consistently higher for the test leathers than for the controls, although not always at significant levels, as shown in Tables III and IV. This is also true for the grain and corium splits of the crust leather but not consistently so for the finished leathers. No consistency is shown for the per cent extension at break for any of the full-thickness leathers, but the grain split values indicate

that elastic tissue removal permits greater extension before breaking. Pounds pull at 25 per cent extension at the end of the first cycle shows that full-thickness side leathers and their corium splits require more force to stretch for the test leathers than for the controls but that the opposite is true for the grain splits. This same effect is shown in Figure 4 for finished side leather.

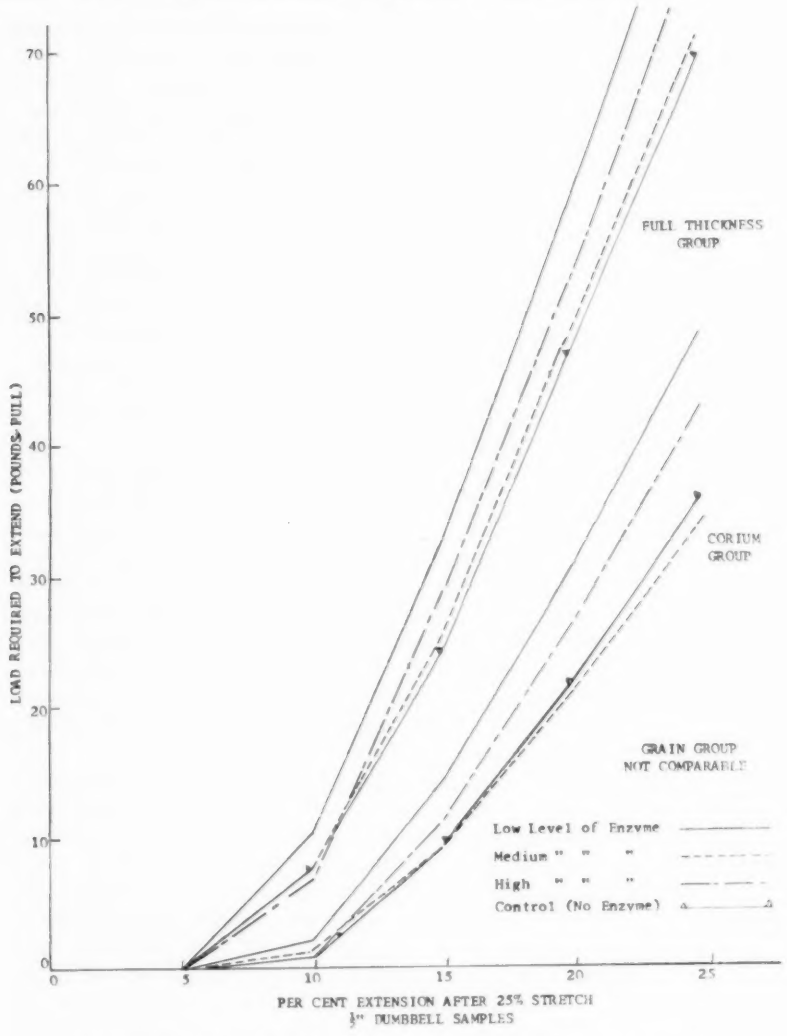

FIGURE 3.—Crusted side leather average stress-strain values (Instron).

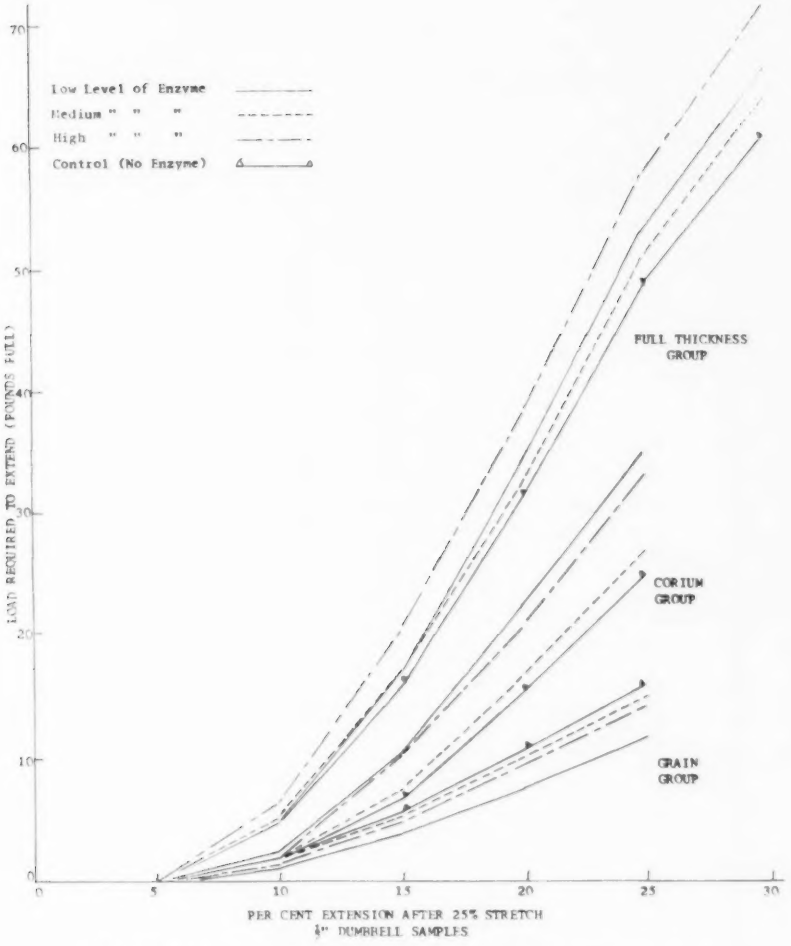

FIGURE 4.—Finished side leather average stress-strain values (Instron).

The plant evaluation of practical physical properties of each side of cowhide leather is shown in Tables V through IX. The average of two or three sorters' opinions is given in the tables. It should be kept in mind as shown by the key at the bottom of each table that higher values mean better temper and break. High values also indicate poorer selection and grain character. Sides 31, 32, and 33 were not part of the main experiment and involved no use of the pancreatic product. They were included to show the effects of

TABLE V

AVERAGE TEMPER EVALUATION BY PLANT SORTERS

Side Leather

Side Number	Level of Pancreatic Product	After Staking (average of 2)		After Buffing (average of 2)		After Finishing (average of 4)	
		Test	Control	Test	Control	Test	Control
1	Low	2.3	4.0	2.8	4.0	1.5	4.3
2	"	4.0	4.0	4.0	4.0	3.8	4.3
3	"	2.8	4.0	3.5	4.0	2.7	4.7
4	"	3.5	3.8	3.5	3.5	3.5	2.5
5	"	4.0	4.0	3.8	4.0	3.8	4.7
6	"	4.0	4.0	3.5	4.0	4.0	3.8
7	"	3.3	4.0	4.0	3.5	2.7	4.2
8	"	4.0	4.0	3.5	4.0	3.5	3.8
9	"	2.8	4.0	3.5	4.0	3.5	5.0
10	"	4.0	3.3	4.0	4.0	3.8	4.3
11	Medium	4.0	4.0	4.0	3.5	4.3	4.2
12	"	3.3	2.8	4.0	3.3	2.7	3.5
13	"	3.3	4.0	2.8	4.0	4.2	2.5
14	"	3.8	4.0	3.5	3.5	2.5	3.7
15	"	3.8	3.8	3.8	3.8	2.8	3.2
16	"	3.5	—	3.5	—	3.2	—
17	"	4.0	4.3	4.0	4.0	4.0	3.8
18	"	3.5	3.3	3.5	2.8	3.0	1.5
19	"	3.5	3.8	2.8	4.0	1.2	2.2
20	"	3.8	4.0	3.8	4.0	3.8	4.3
21	High	3.3	4.0	3.8	4.0	2.3	4.7
22	"	4.0	4.0	4.0	4.0	4.7	4.3
23	"	3.3	4.0	2.8	4.0	3.3	4.5
24	"	4.0	4.0	4.0	4.0	3.5	3.5
25	"	3.5	4.0	3.5	4.0	3.0	4.2
26	"	3.5	4.0	3.5	3.5	2.8	4.0
27	"	3.3	4.0	3.3	4.0	3.8	4.7
28	"	4.0	3.3	4.0	3.8	3.8	4.2
29	"	2.8	4.0	2.8	4.0	3.2	—
30	"	4.0	4.0	4.0	4.0	4.2	4.5
Average		3.57*	3.88	3.59*	3.82	3.31*	3.90
31	Reg.	4.0	4.0	3.8	3.5	3.0	3.8
32	"	3.5	3.8	3.5	3.8	3.5	3.5
33	"	3.3	4.0	4.0	3.5	5.0	4.5

KEY: 1 Very poor; 2 Poor; 3 Fair; 4 Good; 5 Very good.

* Indicates Statistical Significance.

TABLE VI

AVERAGE BREAK EVALUATION BY PLANT SORTERS

Side Leather

Side Number	Level of Pancreatic Product	After Staking (average of 2)		After Buffing (average of 2)		After Finishing (average of 4)	
		Test	Control	Test	Control	Test	Control
1	Low	2.0	3.5	3.0	3.0	2.0	3.0
2	"	2.5	2.5	2.0	2.5	1.0	1.3
3	"	3.5	4.0	3.5	4.0	3.0	4.0
4	"	3.5	4.0	4.0	4.0	2.0	4.0
5	"	2.5	3.0	3.0	3.0	1.3	2.7
6	"	3.5	3.0	3.0	3.0	2.3	2.7
7	"	3.0	3.5	3.5	3.5	3.3	5.0
8	"	4.0	4.0	4.0	4.0	3.3	4.7
9	"	3.0	4.0	3.0	4.0	1.3	4.7
10	"	3.5	3.5	3.5	3.5	2.0	3.7
11	Medium	3.5	4.0	4.0	3.5	3.0	4.3
12	"	3.0	3.5	3.0	3.0	2.0	3.0
13	"	3.5	4.0	4.0	4.0	3.7	4.3
14	"	3.0	3.5	3.0	3.5	1.7	4.3
15	"	3.5	4.0	3.5	3.5	3.7	4.0
16	"	3.5	—	4.0	—	4.7	—
17	"	3.5	3.0	3.0	4.0	3.0	5.0
18	"	3.5	4.0	3.5	3.5	3.0	3.7
19	"	4.0	4.0	4.0	4.0	2.0	3.7
20	"	3.5	3.5	3.0	4.0	2.7	3.7
21	High	3.5	4.0	3.5	4.0	3.0	4.7
22	"	3.5	3.5	3.5	4.0	3.7	4.3
23	"	3.5	3.5	3.5	3.5	3.3	2.7
24	"	3.5	4.0	4.0	4.0	3.0	3.3
25	"	3.0	4.0	3.5	4.0	1.7	4.3
26	"	3.5	4.0	3.5	4.0	3.3	4.0
27	"	2.5	3.5	3.0	3.0	1.0	4.0
28	"	2.5	3.0	3.0	3.5	2.3	4.7
29	"	3.0	4.0	3.0	3.5	3.0	—
30	"	3.5	4.0	4.0	4.0	3.7	4.7
Average		3.24**	3.66	3.38**	3.62	2.55**	3.88
31	Reg.	3.5	3.5	3.0	3.5	3.0	2.7
32	"	4.0	4.0	4.0	4.0	3.3	4.7
33	"	3.0	4.0	3.5	4.0	4.7	5.0

KEY: 1 Very poor; 2 Poor; 3 Fair; 4 Good; 5 Very good.

** Indicates Statistical Significance at .01 level.

TABLE VII

AVERAGE SELECTION EVALUATION BY PLANT SORTERS

Side Leather

Side Number	Level of Pancreatic Product	After Staking (average of 2)		After Buffing (average of 2)		After Finishing (1 only)	
		Test	Control	Test	Control	Test	Control
1	Low	3.0	2.5	1.5	1.5	2.0	3.0
2	"	2.0	2.5	3.0	1.5	2.0	1.0
3	"	3.0	2.0	2.0	3.0	3.0	3.0
4	"	2.5	2.5	3.0	2.0	1.0	1.0
5	"	2.5	1.5	1.5	1.0	1.0	2.0
6	"	2.0	2.5	3.0	2.5	2.0	3.0
7	"	3.0	3.5	2.0	2.5	3.0	4.0
8	"	1.5	1.0	2.5	3.0	2.0	1.0
9	"	2.0	2.0	2.0	1.5	1.0	1.0
10	"	2.0	2.5	2.0	3.0	2.0	2.0
11	Medium	2.5	3.0	2.0	2.5	1.0	3.0
12	"	3.0	2.5	3.0	2.5	2.0	1.0
13	"	2.0	1.5	1.0	1.5	1.0	2.0
14	"	3.0	2.0	3.5	2.5	3.0	4.0
15	"	3.0	3.0	4.0	4.0	2.0	2.0
16	"	3.5	—	3.0	—	2.0	—
17	"	3.0	2.5	2.5	3.0	3.0	1.0
18	"	2.0	2.5	1.5	2.5	2.0	2.0
19	"	4.0	3.0	2.5	2.5	1.0	2.0
20	"	2.0	1.5	2.5	1.5	1.0	1.0
21	High	3.0	3.0	2.5	3.0	3.0	3.0
22	"	2.0	2.5	1.5	2.0	1.0	2.0
23	"	3.0	2.0	2.5	2.0	2.0	2.0
24	"	2.0	3.0	1.5	3.0	1.0	3.0
25	"	3.0	3.5	2.5	3.5	2.0	3.0
26	"	3.5	2.5	4.0	3.0	3.0	2.0
27	"	3.0	2.5	2.5	2.0	1.0	3.0
28	"	3.0	1.5	1.5	1.0	1.0	1.0
29	"	2.5	3.0	1.5	3.0	1.0	—
30	"	3.0	1.5	2.0	1.5	2.0	1.0
Average		2.62*	2.38	2.31	2.38	1.82	2.11
31	Reg.	2.0	2.5	2.0	1.0	2.0	3.0
32	"	2.5	2.0	2.5	3.0	3.0	3.0
33	"	3.0	1.0	1.5	1.5	2.0	1.0

KEY: 1 to 4 are best to reject.

* Indicates Statistical Significance.

TABLE VIII

DRAWN GRAIN AND VEININESS EVALUATION BY PLANT SORTERS

Side Leather in the Crust

Side Number	Level of Pancreatic Product	1st Sorter		2nd Sorter	
		Test	Control	Test	Control
1	Low	DG	DG	3.0	3.0
2	"	DG	DG	3.0	4.0
3	"	DG	DG	2.0	1.0
4	"			2.0	1.0
5	"	DG	DG	5.0	2.0
6	"		DG	3.0	2.0
7	"	DG		2.0	3.0
8	"			1.0	2.0
9	"	DG	DG	3.0	2.0
10	"	DGV	DG	2.0	2.0
11	Medium	DG		2.0	2.0
12	"	DG	DG	4.0	3.0
13	"	DG		2.0	1.0
14	"			1.0	2.0
15	"	DGV	DG	3.0V	2.0
16	"	V	No Sample	1.0	No Sample
17	"			3.0	1.0
18	"	DG		2.0	1.0
19	"			2.0	1.0
20	"	DG		3.0	2.0
21	High	DG		3.0	1.0
22	"	DG	DG	3.0	3.0
23	"	DG		3.0	3.0
24	"			2.0	1.0
25	"	DG	DG	5.0	2.0
26	"	DG		3.0	2.0
27	"	DGV		5.0	3.0
28	"	DG		5.0	4.0
29	"	DG	DG	3.0	2.0
30	"	DGV		2.0	1.0
Average				2.86*	2.03
31	Reg.	DG		2.0	2.0
32	"	DG		2.0	1.0
33	"	DG		3.0	1.0

KEY: 1 to 5 increasing drawn grain.
* Indicates Statistical Significance.
DG: Drawn Grain
V: Prominent Veins

TABLE IX

AREA OF LEATHER

Finished Side Leather

(Square feet per side)

Side Number	Level of Pancreatic Product	Test	Control
1	Low	17.50	18.00
2	"	19.50	16.50
3	"	20.50	19.25
4	"	20.75	22.50
5	"	18.00	18.00
6	"	18.50	16.50
7	"	17.00	18.75
8	"	21.50	17.25
9	"	19.50	20.50
10	"	18.00	16.50
11	Medium	15.00	18.00
12	"	20.00	16.50
13	"	17.25	18.00
14	"	19.00	19.00
15	"	19.25	21.00
16	"	19.50*	No Sample
17	"	17.25	15.25
18	"	20.25	19.50
19	"	16.25	16.25
20	"	20.50	20.00
21	High	19.50	18.00
22	"	16.25	16.25
23	"	19.25	18.00
24	"	20.00	19.50
25	"	18.50	20.50
26	"	20.50	21.00
27	"	18.25	19.50
28	"	19.00	17.25
29	"	16.25*	No Sample
30	"	19.25	20.25
Average		18.79	18.48
31	Reg.	18.50	17.50
32	"	17.00	19.00
33	"	16.25	16.75

*These sides not considered in the average.

complete deliming as used for all the test and control sides as compared with the regular bating procedure. Values for these sides were not used in any of the interpretations which follow. Rank analysis of differences between pairs over the whole population was used to determine significance.

As shown in Table V the plant sorters decided that temper was better (firmer) for control sides in the crust after staking, after buffing, and for the finished leather. Laboratory measurement of temper as shown in Tables III and IV showed this same tendency but not at significant levels. It is possible that had we had the complete side distribution as used for previous correlation studies we might have agreed more exactly.

In Table VI the results show that break was better for the control sides than for the test sides. Laboratory measurement of break as shown in Tables III and IV tended to show the opposite although not usually at significant levels.

Plant evaluation of selection is concerned mostly with natural defects but may be influenced by veins, fat wrinkles, ribbiness, rough grain, etc., which may have been affected by removal of elastic tissue. A significant difference in the results shown in Table VII is found only for the crust leather after staking. In this leather the control sides gave a better selection than the test sides, but for the other two groups the opposite was true, although not at significant levels.

In Table VIII the two sorters used different ways to express the degree of drawn grain, but in both cases it is obvious that the control sides had less drawn grain than the test sides. This may reflect the extra drumming which the test sides received during pancreatic product treatment. Only a few sides were noted (with the letter V) as having prominent veins, but these were all among the test sides.

TABLE X

ANALYSIS OF FINISHED LEATHERS

Side Leather

	Control (Regular Enzyme, Special Deliming)	Pancreatic Product Level		
		Low	Medium	High
Moisture	13.07	13.44	13.16	13.21
Chloroform Extract (MFB)	3.89	3.93	3.83	4.07
Hide Substance (MFB)	81.00	80.19	78.95	78.48
Total Ash (MFB)	4.69	4.86	4.73	4.75
Chrome Oxide (MFB)	4.10	4.14	4.04	4.04
pH	3.40	3.40	3.43	3.44

The area of all the sides was measured, and the results are shown in Table IX. No significant difference was shown between the test and the control sides. The assumption was made that the two sides in each pair had the same area before pancreatic product treatment.

Results of the chemical analysis of the leathers produced in the plant tests are shown in Table X. It is noted that there is little difference in chemical composition of the regular production side leather in comparison with the chemical composition of the side leathers which were prepared from low, medium, and high pancreatic product treatments.

CONCLUSIONS

The removal of elastin from hides under the specific conditions used affected the properties of the leather produced.

1. The evidence from plant grading shows that treatment with the special pancreatic product reduces the temper of side leather, although this is not borne out by laboratory testing of a single position in each side.

2. Plant gradings of side leather agree that treatment with the special pancreatic product produces a coarser break than does regular bating practice.

3. Plant gradings of side leather agree that treatment with the special pancreatic product produces more drawn grain than does regular bating practice.

4. Physical tests indicate that treatment with the special pancreatic product has improved fiber strength of side leather as shown by stitch tear, tensile strength, and increased force required to stretch the leather.

5. Physical tests indicate that treatment with the special pancreatic product has improved the grain properties of side leather as shown by higher Mullen pressure at grain crack and by less force required to stretch the grain than for either the corium split or the full thickness of the leather.

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INSULATED BOOT

Increased foot protection for military personnel operating in Arctic temperatures will be afforded by a new white insulated rubber combat boot developed by the Army Quartermaster Corps. The boot, which will be worn with only one pair of socks, may replace the cold-dry mukluk boot and the Arctic felt boot, both of which required several pairs of wool socks. It uses the vapor barrier principle in sealing three layers of wool fleece in the upper and two layers of felt in the midsole between inner and outer rubber layers. The seal prevents sweat and outside moisture from wetting the fleece and thereby destroying the boot's insulating properties. Each boot has a self-closing air-release valve for equalizing air pressure that may build up inside the boot's insulation, thus preventing swelling and constriction of the foot when the boot is worn at high altitudes. The new boot weighs two pounds less than the old boot with its combination of sockgear and felt insoles. The boot will increase foot protection, provide greater durability, foot support, and traction and will be compatible with individual oversnow equipment such as skis and snowshoes. It has functioned adequately in temperatures reaching 102 degrees below zero.
—*Retired Personnel Newsletter*, Sixth United States Army, July, 1960.

STRATIGRAPHIC DISTRIBUTION OF CARBOHYDRATE, HEXOSAMINE, AND HYDROXYPROLINE IN CATTLEHIDES*

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ABSTRACT

A precision slicing technique was employed to cut consecutive slices of equal thickness parallel to the grain surface of cattlehides. Quantitative determinations of carbohydrate, hexosamine, and hydroxyproline were made on the slices. The actual weight of all three components was lower in the grain slices than in the corium. However, when calculated on a dry-weight or nitrogen-content basis, the carbohydrate and hexosamine appear more concentrated in the grain region. Hydroxyproline follows the distribution of dry weight and nitrogen content more closely but indicates that a large part of the nitrogen content of the grain is not due to collagen. A steerhide and a cowhide were studied.

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INTRODUCTION

The stratigraphic study of the chemical composition of cattlehides makes possible the quantitative measurement of variations in concentration of constituents through the thickness of a hide. Therefore, it is possible to amplify the qualitative or semiquantitative observations obtained by histological studies and extend studies to reactions not possible by histological techniques. Roddy (1) recently reviewed the known structure of animal hides which was obtained chiefly through histological studies. Comparatively few stratigraphic studies have been made, but they have added considerably to the knowledge of the structure and reactivity of animal hides.

Stubbings and Theis (2) demonstrated through a stratigraphic study of swelling phenomena that the grain protein was less dense than the corium

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protein and this variation in density resulted in differences in swelling under various conditions. A similar difference in apparent density between the grain and the center of the corium was obtained by Mellon *et al.* (3) in stratigraphic studies of the distribution of dry matter and nitrogen in a steerhide. These studies indicated that the center of the corium was almost twice as dense as the grain region.

The stratigraphic studies by McLaughlin and Theis (4), Strandine *et al.* (5), and Kritzinger and Van Zyl (6) show a higher concentration of moisture in the grain region than in the center of the corium. Whether this additional water is free and can be squeezed out or is bound in some rigid structure such as a gel has not been determined. Two possible gel systems are the mucoid materials and the nonfibrous proteins. Reed (7) discussed the histological distribution of mucoids and showed that, although they existed through the entire thickness of the hide, there were higher concentrations in the grain region. Thus the presence of mucoid gels could explain not only the high water content of the grain region but also the high water content throughout the hide. Stubbings (8) showed a similar distribution for the nonfibrous proteins which could be solubilized by 10 percent sodium chloride solutions. Therefore, the nonfibrous proteins as well as the mucoids appear to be distributed similarly to the water content of a hide.

The present study was undertaken to measure the distribution of two components of mucoid materials—carbohydrate and hexosamine—through the thickness of a hide and to compare their concentration with the content of dry matter, nitrogen, and collagen.

EXPERIMENTAL PROCEDURE

Preparation of Samples—The steerhide samples were taken from the same hide used in the previous study of dry matter and nitrogen content (3). The cowhide samples were from the bend portion of a hide from a ten-year-old cow. Details of the treatment, which was the same for both hides, are given in the previous study. The fresh hides were washed, fleshed, and frozen for storage. For each run a small area of hide was thawed, shaved, soaked overnight, then cut into pieces approximately one and a half centimeters square. Approximately eight of these pieces were sliced to obtain the analytical samples. The flesh side of each piece was frozen to the microtome stage and sliced parallel to the grain surface into slices which were 0.1 mm. thick. If a cut across the entire piece was not obtained by the fourth slice, the entire piece was rejected. Five consecutive slices were pooled and called a layer, and each layer was analyzed separately. The layers are numbered from the hair side.

Analytical Methods—The slices representing each layer were dehydrated with several changes of acetone and dried to constant weight at 45° C. in a

vacuum oven through which a stream of air, dried over magnesium perchlorate, was circulated. Details of this procedure and of the Kjeldahl nitrogen determination are given in reference 3. It is unfortunate that the hydrolysis conditions required to obtain maximum values for carbohydrate, hexosamine, and hydroxyproline are considerably different. This necessitated separate runs for each material and increased the number of dry weight and nitrogen values which had to be made.

Most satisfactory results for carbohydrate were obtained by hydrolyzing the sample for four hours in 4 normal hydrochloric acid (9). Carbohydrate was determined on this hydrolyzate by the anthrone method of Trevelyan and Harrison (10). The data are expressed as milligrams of glucose by calculation from a standard curve for glucose, although other sugars may also be present.

For the hexosamine determination by the method of Boas (11), the slices were hydrolyzed for sixteen hours in 2 normal hydrochloric acid. Glucosamine was used as the standard, although other hexosamines may also be present in the hydrolyzate.

For the hydroxyproline determination by the Bowes (12) modification of the Neuman and Logan method, the slices were hydrolyzed for sixteen hours in 6 normal hydrochloric acid. A standard curve was run with each determination, although the variations in the curves from determination to determination were slight.

RESULTS AND DISCUSSION

Previous studies (3) on the stratigraphic distribution of dry matter and nitrogen in steerhides showed that the concentration (weight per unit volume) of dry matter and nitrogen is twice as great in the corium region as it is in the grain region. Because of this difference in concentration of dry matter, comparisons made on a dry-weight basis may differ considerably from comparisons made on a unit-volume basis. Since each layer analyzed for a given run has the same volume, the actual weights within any single run which are given in Tables I, II, and III reflect the variations in concentration for that run. The weights of carbohydrate, hexosamine, and hydroxyproline divided by the weights of either the dry matter or nitrogen produce a ratio which is also useful for comparison.

Table I contains the experimental values obtained in the carbohydrate study. Runs 1 and 2 are on the steerhide, and run 3 is on the cowhide. Figure 1 graphically reproduces the actual weight data for runs 1 and 3 so that a visual comparison can be made with subsequent figures. The concentration of carbohydrate in the grain region is less than in the corium region. In this manuscript the boundary between the grain region and the corium region, which occurs at about the base of the deepest hair follicles, comes between

TABLE I

THE DRY WEIGHT (Wt), NITROGEN (N), AND CARBOHYDRATE (C) CONTENT OF STRATIGRAPHIC LAYERS OF ACETONE EXTRACTED CATTLEHIDES

	Run 1			Run 2			Run 3		
Layers*	Wt. mg.	N mg.	C mg.	Wt. mg.	N mg.	C mg.	Wt. mg.	N mg.	C mg.
1	112	18	0.49	132	22	0.69	97	16	0.55
2	162	27	.68	168	28	.82	143	23	.66
3	184	32	.69	193	32	.70	136	22	.56
4	224	38	.68	269	45	.90	198	34	.54
5	275	48	.75	322	56	1.02	249	43	.63
6	288	51	.79	319	56	1.02	305	54	.82
7	310	54	.80	331	58	1.12	331	57	.96
8	301	53	1.04	348	61	1.16	317	56	.83
9	320	56	.98	350	62	1.29	318	56	1.01
10	317	55	.91	322	57	1.25	301	53	.91
11	316	55	1.03	316	56	1.18	243	42	.84
12	335	58	.98	300	54	1.06	†	†	†
13	336	58	.95	200	35	.88	†	†	†
R‡	1022	179	3.68	429	76	2.05	254	44	1.13

*Numbered from hair surface.
†This specimen was several layers thinner.
‡The residue which contains the last full layer plus the remaining partial layer.

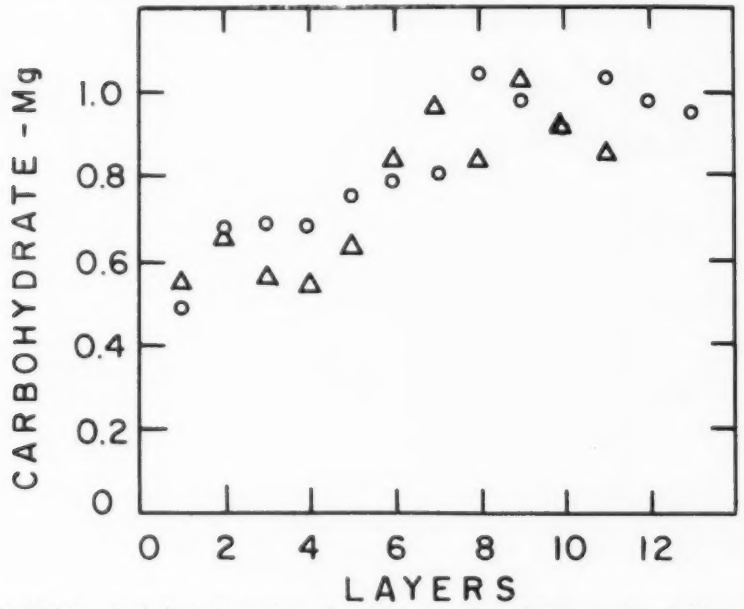

FIGURE 1.—Carbohydrate content of serial layers of cattlehides numbered from the hair surface: ○ a steer, △ a 10-year-old cow.

TABLE II

THE DRY WEIGHT (Wt), NITROGEN (N), AND HEXOSAMINE (H) CONTENT OF STRATIGRAPHIC LAYERS OF ACETONE EXTRACTED CATTLEHIDES

Layers*	Run 4			Run 5			Run 6		
	Wt. mg.	N mg.	H mg.	Wt. mg.	N mg.	H mg.	Wt. mg.	N mg.	H mg.
1	242	37	1.11	153	25	1.12	125	21	.74
2	333	51	1.63	225	38	1.28	174	29	.85
3	452	71	1.04	305	48	1.23	167	29	.85
4	547	89	1.11	352	57	1.05	197	35	.68
5	648	104	1.20	429	74	1.36	362	56	.82
6	643	98	1.24	395	69	1.24	344	61	.82
7	654	101	1.20	443	78	1.33	375	67	.98
8	621	98	1.29	426	74	1.30	413	74	1.16
9	643	104	1.37	443	78	1.39	364	65	.94
10	585	95	1.42	408	72	1.35	371	66	1.06
11	560	90	1.44	404	71	1.36	†	†	†
12	528	84	1.33	368	65	1.43	†	†	†
R‡	836	141	2.17	833	143	3.38	672	117	2.39

*Numbered from hair surface.
†This specimen was several layers thinner.
‡The residue which contains the last full layer plus the remaining partial layer.

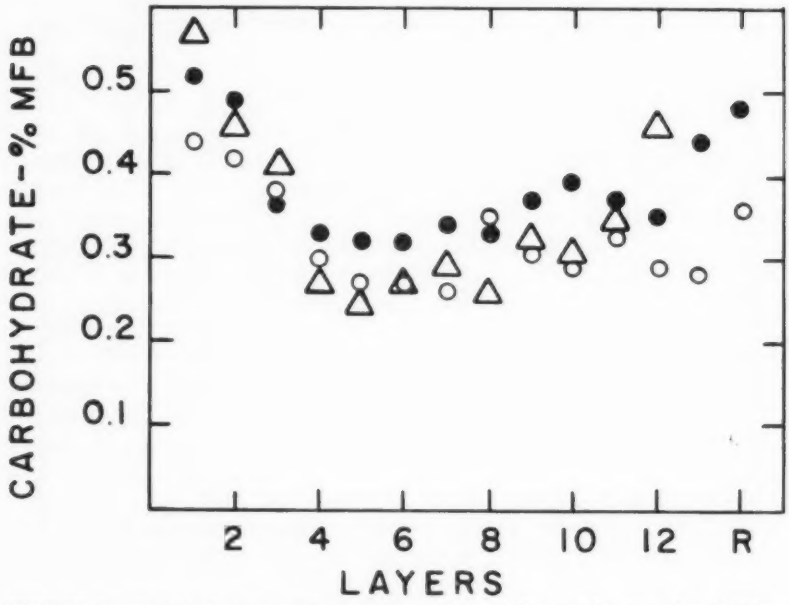

FIGURE 2.—Carbohydrate content on a dry-weight basis for serial layers of cattlehides: ● and ○ a steer, △ a 10-year-old cow. R is the flesh side residue.

TABLE III

THE DRY WEIGHT (Wt), NITROGEN (N), AND HYDROXYPROLINE (HP) CONTENT OF STRATIGRAPHIC LAYERS OF ACETONE EXTRACTED CATTLEHIDES

Layers*	Run 7			Run 8			Run 9		
	Wt. mg.	N mg.	HP mg.	Wt. mg.	N mg.	HP mg.	Wt. mg.	N mg.	HP mg.
1	88	15	7	92	15	7	72	12	5
2	166	28	14	120	20	11	102	17	9
3	207	35	19	160	28	15	118	20	10
4	280	48	34	189	33	22	145	25	17
5	323	56	39	230	40	27	171	29	21
6	379	66	43	202	36	24	179	32	20
7	413	72	48	225	40	29	187	33	22
8	376	66	49	275	49	35	202	36	26
9	387	67	45	228	40	23	212	38	28
10	422	73	50	239	42	25	184	33	23
11	377	66	42	250	44	27	199	35	25
12	225	39	24	251	44	31	194	34	24
13	145	25	16	89	16	10	157	28	16
R‡	524	88	56	399	70	45	359	62	39

*Numbered from hair surface.
‡The residue which contains the last full layer plus the remaining partial layer.

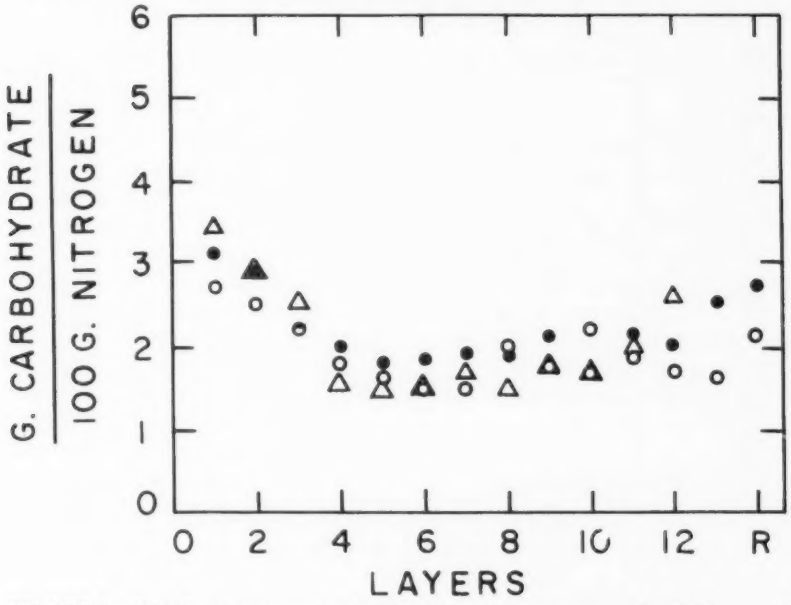

FIGURE 3.—Carbohydrate content related to the nitrogen content of serial layers of cattlehides: ● and ○ a steer, △ a 10-year-old cow. R is the flesh side residue.

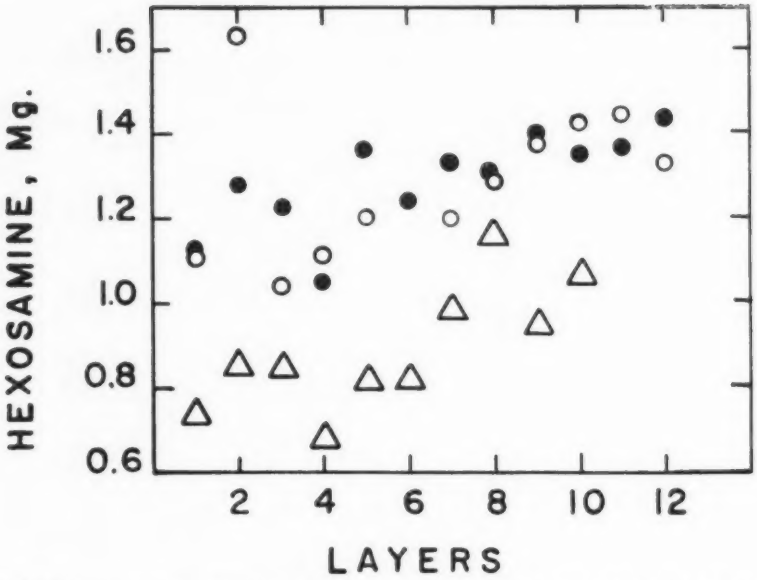

FIGURE 4.—Hexosamine content of serial layers of cattlehides numbered from the hair surface: ● and ○ a steer, △ a 10-year-old cow.

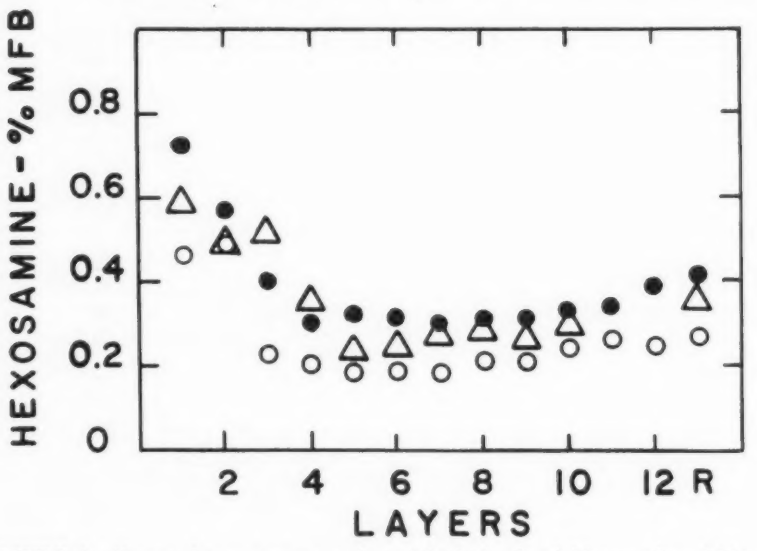

FIGURE 5.—Hexosamine content on a dry-weight basis of serial layers of cattlehides: ● and ○ a steer, △ a 10-year-old cow. R is the flesh side residue.

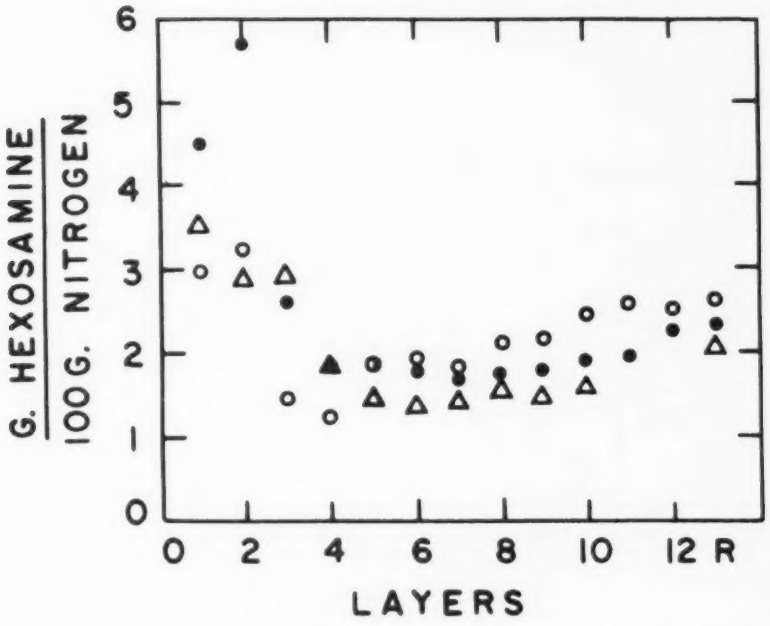

FIGURE 6.—Hexosamine content related to the nitrogen content of serial layers of cattlehides: ● and ○ a steer, △ a 10-year-old cow. R is the flesh side residue.

the third and fourth layers. Since the steer was about three years old and the cow was ten years old at slaughter, the sex or the age of the animal does not appear to alter the pattern. The carbohydrate content as a percent of the dry weight, which is plotted in Figure 2, gives a contrasting curve with high values in the grain region and lower values in the corium region. A similar curve, Figure 3, is obtained when the carbohydrate content associated with 100 grams of total nitrogen is plotted. We must bear in mind that Figures 2 and 3 do not show a higher concentration of carbohydrate in the grain region. The values are high only because the dry weight and nitrogen are low in the grain region. If any carbohydrate constituents are responsible for the high water content of the grain layers, these constituents must be different or react differently in the grain region than in the corium.

The results of the hexosamine study are given in Table II. The actual weight of hexosamine found in each slice is plotted in Figure 4. The content of hexosamine is slightly lower in the grain region than it is in the corium region. The triangular points representing the data on the 10-year-old cow are low only because fewer pieces were sliced for this experiment. In Figure 5,

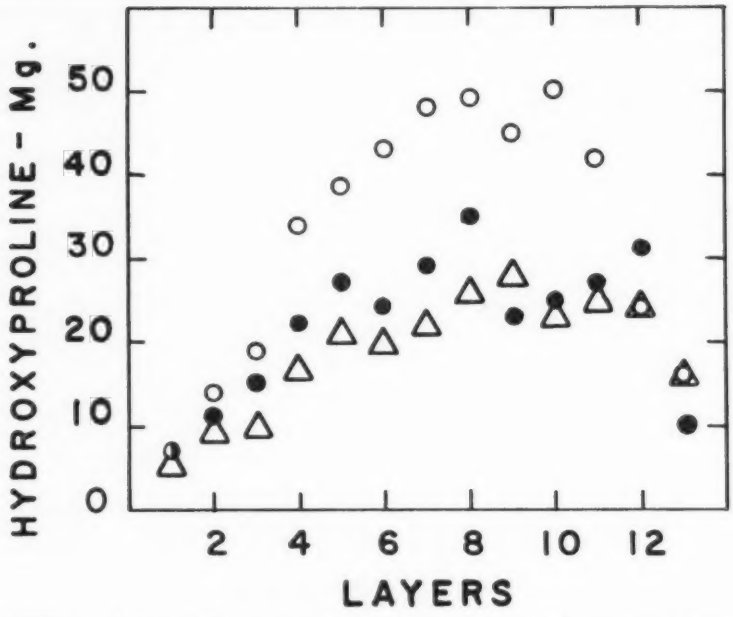

FIGURE 7.—Hydroxyproline content of serial layers of a steerhide numbered from the hair surface: ●, ○, and △ are from closely related areas near the center of the hide.

which shows the variation of the hexosamine content as a percent of the dry weight, the value is high for the grain region and practically constant throughout the corium region. Similar results are obtained when the grams of hexosamine associated with 100 grams of nitrogen content are plotted as shown in Figure 6. Again we must bear in mind that Figures 5 and 6 do not show a higher concentration of hexosamine in the grain region. The values are high only because the dry weight and nitrogen are low in the grain region. Therefore, if any hexosamine-containing materials are responsible for the high water content of the grain layers, these materials must be different or react differently in the grain region than in the corium.

These findings on the distribution of carbohydrate and hexosamine containing materials appear to be contradictory with histological findings. Nevertheless, the facts obtained by both methods can be reconciled by recognizing the difficulties involved in making quantitative estimations from histological observations. It is true that staining reveals localized high concentrations of mucoid materials in the papillary and dermal-epidermal regions, and these can give the impression that the grain layer is exceptionally rich in these materials.

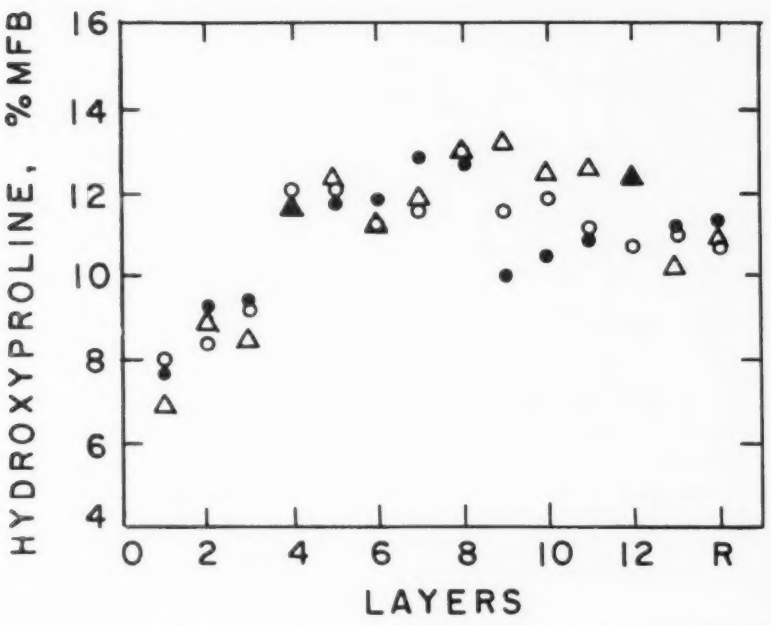

FIGURE 8.—Hydroxyproline content on a dry-weight basis for serial layers of a steerhide: ●, ○, and △ are from closely related areas near the center of the hide, R is the flesh side residue.

The data for the hydroxyproline study are presented in Table III. Only the steerhide was used in this study. Figure 7 shows that the actual weight of hydroxyproline content is very much less in the grain region than in the corium. Even when the hydroxyproline is considered as a percent of the dry matter, Figure 8, the values are lower in the grain region than in the corium. This is also true when grams of hydroxyproline associated with 100 grams of nitrogen content are plotted, Figure 9. The maximum value reached about the center of the corium is just slightly below the value of 75 found in many samples of purified collagen. This is a very good indication that the protein in the center of the corium is mostly collagen. The very low value in the grain region emphasizes that much of the protein in this region is not collagen. The concentration of these noncollagenous proteins changes rapidly in the region between the grain and the corium. This change is similar to the change in the water content, and therefore it appears that the noncollagenous proteins could be the components responsible for retaining the high proportion of water in the grain region.

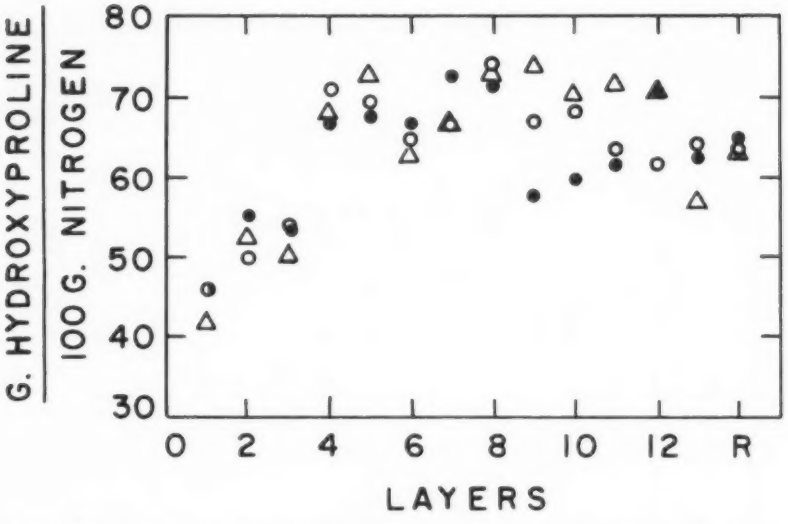

FIGURE 9.—Hydroxyproline content related to the nitrogen content of serial layers of a steerhide: ●, ○, and △ are from closely related areas near the center of the hide. R is the flesh side residue.

CONCLUSIONS

The concentration of both carbohydrate and hexosamine on a volume basis of fresh hide is less in the grain region of cattlehides than in the corium region. This was found for the hides of both a steer and a ten-year-old cow. Therefore, unless there is a difference between the carbohydrates found in the grain region and the corium, it is unlikely that these materials are the cause of the high hydration of the grain region.

The concentration of hydroxyproline is very low in the grain region. The ratio of hydroxyproline to nitrogen content is also low. Therefore, there is less collagen and more noncollagenous proteins in the grain region than in the corium. The change in concentration of these noncollagenous proteins follows the change in moisture content which occurs through the thickness of a hide. The hydration of these proteins may explain the high moisture content of the grain region of fresh cattlehides.

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DISCUSSION

Dr. Robert M. Lollar (Armour Leather Company): Again we see a presentation of one of these carefully prepared papers full of theoretical knowledge which we have come to associate with the Eastern Regional Research Laboratory. As one who is today quite interested in the practical aspects of the development of leather chemistry, I should like also to record my appreciation of the fact that today we are becoming more and more dependent upon laboratories such as this for this theoretical work which we need as a basis for our practical developments.

I think it is quite important that we continue to have that base line of theoretical information on which we can make our practical developments of the future.

Turning now to the specific paper and going back to some of the work that I was conducting in the Tanners' Council Laboratories in Cincinnati (before I left there a couple of years ago), there are a couple of points in the paper that we might comment on first.

The first one specifically concerns itself with the question of the hydrolysis conditions. Dr. Mellon said that it was impossible to use the same conditions for all analyses. I would like him to comment on the criteria which he used to select the hydrolysis conditions in each case.

Dr. Mellon: In the analysis for carbohydrates and hexosamine, we had to make a compromise between two facts. One is that these materials are bound in certain combinations in the material and we have to try to hydrolyze the material to free these compounds. On the other hand, the acids and the temperature which are used for the hydrolysis cause a decomposition of these materials and convert them into other materials which would not be measured with the method of analysis. Since we have no alternative, we work out the conditions which will give us a maximum value. The amounts of acid and times of hydrolysis which we have used give us a maximum value.

This would bear some relationship to the actual concentration of the material in the hide, but it is not an excellently proved value because there is a very good possibility that we have not completely freed these materials from the combinations they are in; and also, in the length of time that we have tried to separate them from these combinations, some material has become decomposed. So the values we have are somewhat less, perhaps, than the total amount present in the hide.

If we could find a method of analyzing for these materials without hydrolyzing the hide, I am pretty sure the values would be higher, but we feel the values that we have presented are proportionate to the content in the hide.

DR. LOLLAR: Did you, in the course of your work to determine the optimum conditions, consider ion exchange resin hydrolysis?

DR. MELLON: We did not consider it. We used the resin column to purify the hexosamine before we determined it, but we did not consider using the resin in place of the acid for the hydrolzying medium.

DR. LOLLAR: Of course, you are well aware that these resins in their acid form have been used as hydrolysis media. In some of the work that we were doing at Cincinnati when I left, we did find some evidence on the basis of paper chromotography of the hydrolysates, and of recovery values, that it might be possible that better recoveries would be obtained if resin hydrolysis were used in place of straight acid hydrolysis.

I think perhaps we might need to consider this approach if we were attempting to get absolute recoveries. This may perhaps be another lead to this point that you alluded to in your discussion—that we may not have maximum recovery.

DR. JOHN H. HIGHBERGER (United Shoe Machinery Corporation): Was the method you used for hexosamine the Boas Method?

DR. MELLON: Yes.

DR. PETER R. BUECHLER (Rohm & Haas Co.): A lot of this work Dr. Mellon is doing is dependent on the distribution of water in the steerhides and indicates a large amount in the grain area.

Since, in his analytical work, he and Mr. Viola had to determine the moisture content of the samples, I wonder if it would not be possible for him to discuss with us in these very same hides the water distribution on the same basis that he has presented the distribution of hexosamine, collagen, and carbohydrate.

DR. MELLON: The main reason we have not attempted to do this is because we use a fairly large area of tissue on the microtome stage, and in order to freeze this tissue on the stage so that we can slice it through the entire thickness of the hide, we have to freeze a little water on to the stage first so that our slicing blade will not hit the metal part of the freezing component. We usually slice 12 to 13 layers of tissue at 5 slices to a layer, which makes somewhere around 60 slices to a piece. And if we get two-thirds of the way through and then knock the piece off the stage, we have to throw away all of those slices. In order to keep our sample on the stage until we have completely sliced it, we build a ring of water or ice up around the sample to add this additional prop to the sample.

Each slice, as we slice it off, has this little ring of ice around the outside. And since the slices are quite thin, it would be quite difficult to remove this ring of ice and therefore obtain a sample which contained only the tissue. We feel, therefore, that we would be introducing as much error if we tried to take these slices, melt the ice, and then blot them to obtain only a tissue specimen, as we would by basing all our studies on the dry weight or the actual volume of tissue which we are cutting.

DR. BUECHLER: This point is very well taken. However, I wonder if, on the same hide, you could not take a very small section, such as we occasionally did, of the raw stock, and freeze it just using the moisture of the tissue itself? Of course, you have washed it and I suppose this would introduce another problem.

DR. MELLON: Since we do soak this hide in water overnight to make sure the water is uniformly distributed through the hide, we have to consider these moisture relationships as being maximum values that the hide could obtain. I feel, myself, that the hide on the animal's back does not contain quite as much moisture as the samples that we have been analyzing.

JOSEPH JANY (Ontario Agricultural College): Dr. Mellon, your hydroxyproline and hexosamine determinations were influenced to a certain extent by the severe conditions of the strong hydrolysis to which these substances were subjected. As this circumstance is a rather disturbing factor, I wonder whether or not you ever tested solutions of chemically pure hydroxyproline or hexosamine under the same severe conditions, in order to determine to what extent they may be attacked and to what extent your results may be influenced by this fact.

DR. MELLON: All we have done is to determine the values on material already in the hide by varying the condition of hydrolysis to obtain the maximum value. We ran the purified hexosamine to establish what our colori-

metric base line should be, but we did not run those materials through the hydrolysis procedure.

MR. JANY: Then I want to ask about the moisture determination. It is quite a problem generally, because if the substance is not disintegrated, then it is very hard to get a stable moisture content. If it is disintegrated, then in disintegration we lose some moisture. So I wonder if you used the xylene method where you don't have this problem?

DR. MELLON: We have developed a moisture determination which we have used for a number of years in the protein group of our Laboratory. It involves a vacuum oven. The one innovation is that instead of just sealing the oven and pumping on it with a vacuum pump, we pass through the oven a stream of air which has been dried by passing through magnesium perchlorate, so that the air stream flowing through the oven has practically zero relative humidity. In the samples which we have been studying—and this holds for a large number of proteins—we can get a constant value which holds for temperatures anywhere from 40° to 70° or 80°. We can put the sample in and obtain a value at 40°, and we can raise the temperature to 70°, and we will not have any difference in this value. If you go to much higher temperatures with some proteins, you will obtain some sort of a decomposition which will give you different readings. So we limit our dry weight determinations to the temperature between 40° and 70°, using the flowing stream of dry air to carry away any moisture which would be in the sample. Since we can get a reproducible value over this temperature range, we feel that our moisture values are about as constant as anyone can determine. We feel they are much more reproducible than if you determine moisture in an oven at 105° or higher.

Papers contained in *JALCA* 25 years ago this month (November, 1935, vol. 30, no. 11) included A Study of Keratin of Leonor Michaelis, from the Laboratories of the Rockefeller Institute for Medical Research, New York; Some Notes on the Construction and Operation of an Experimental Rocker Section by William P. Doelger, Dept. of Leather Research, Foundation Tanners' Council of America, Institute of Scientific Research, University of Cincinnati, Cincinnati, Ohio; and Comparative Wear of Chrome, Vegetable and Retanned Sole Leather by R. C. Bowker and W. E. Emley.

LIFE LINES

Brief Biographies of Our Contributors

DR. EDWARD F. MELLON—See the February, 1960, *Journal*.

DR. JOSEPH NAGHSKI since 1955 has been Head of the Hides, Tanning Materials and Leather Section of the Eastern Utilization Research and Development Division of the U. S. Department of Agriculture. He received the B.S. degree from Cornell University, the M.S. degree from the University of New Hampshire, and the Ph.D. degree from Pennsylvania State University. He joined the staff of the United States Department of Agriculture's Eastern Regional Research Laboratory in 1941 where he has carried out research in various fields which include the chemistry and microbiology of tobacco fermentation, the chromatography of tobacco alkaloids, the chemistry of flavonoids, the chemistry and microbiology of maple sugar products, and microbiological processes for recovery of natural rubber. He is coauthor of a recent book entitled *Rutin and Related Flavonoids*.

CONRAD L. ORNES—See the March, 1960, *Journal*.

WILLIAM T. RODDY—See the March, 1960, *Journal*.

SAMUEL J. VIOLA—See the February, 1960, *Journal*.

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Proceedings, Reports, Notices, and News

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Notice to Authors

Authors are requested to introduce each paper submitted to the *Journal* by an abstract of the article. Articles should also be accompanied by a brief biography of the author(s) for inclusion in the "Life Lines" feature in the *Journal*. Unnecessary correspondence will also be avoided if a notation is attached to the copy indicating where the author desires galley proofs to be sent.

Obituary

RALPH W. FREY, SR.

Members of ALCA will be saddened by the death of Ralph W. Frey, Sr., at his home near Washington, D. C., on August 22, at the age of 71.

Mr. Frey was a very active member of ALCA for many years, joining the Association in 1915 and becoming a Life Member in 1955. He was president of our Association from 1930 to 1932 and chairman of a number of committees entitled Division of Analytical and Control Methods.

Mr. Frey graduated from George Washington University with a Bachelor of Science degree in chemistry in 1912. He worked briefly for a steel company and then joined the Department of Agriculture in 1914. With the exception of a short interlude in 1919 with J. H. Heald & Company, manufacturers of extracts, he served with distinction in the Hides, Tanning Materials and Leather Section of the Bureau of Chemistry and Soils for 29 years until his retirement due to ill health in 1943.

Preferring to stay in Washington following his recovery, he joined the Washington Suburban Sanitary Commission in 1947 and retired in 1958.

He was a prolific research worker and writer. His first paper on leather chemistry was published in 1917. By 1940 he had published 90 papers in the fields of the preservation of hides, the cause and prevention of red rot in vegetable-tanned leather, domestic sources of vegetable tannins, and methods for the analysis of tannins. In 1942 he received the Alsop Award for these outstanding contributions to leather chemistry.

ABSTRACTS

The Preparation of Water-soluble Leather Oiling Materials by Addition of Bisulfite to Unsaturated Oils. III. The Theory of Oxidative Sulfiting of Unsaturated Oils. A. Küntzel and L. K. Schwörzer. *Das Leder*, **11**, 60–66 (1960); see *JALCA*, **53**, 649 (1958).—China wood oil, oiticica oil, and Ilinol-Standard (an isomerized linseed oil), which have conjugated double bonds, react to only a very slight degree with bisulfite to form sulfonic acids. Cod and sperm oils have isolated double bonds (double bonds separated by two or more single bonds), but by isomerization they can be converted to compounds with conjugate bonds. After conversion, however, the oils were much less reactive with bisulfite; for example, sulfited, isomerized cod oil contained only 3.1% fixed SO_2 instead of 15.9% as found in sulfited but not isomerized oil. Castor oil and ricinoleic acid were dehydrated by heating in a vacuum (15 mm. mercury) at 240°–50°C. for 45 min. with sulfuric acid and anhydrous sodium sulfate. The resulting ricinene oil and acid esters of the latter reacted with bisulfite to form products that emulsified in water. Although the dehydrated oil contained conjugated double bonds, isolated double bonds were also present. For a theory of sulfiting of unsaturated oils the following experimentally established facts must be considered. Sulfite only adds onto fatty acids with isolated double bonds. The sulfiting reaction is possible only in the presence of atmospheric oxygen. Activation of individual double bonds, which results in attachment of sulfite, is caused by alpha carboxyl or hydroxyl groups. Isolated and conjugated bonds do not react in the same way. Conjugated bonds are known to react with oxygen more rapidly than isolated bonds, and in the reaction polymeric peroxides are formed. A hydroperoxide theory of autooxidation of isolated double bonds has been proposed by Rieche and developed by Farmer (*Trans. Farady Soc.*, **38**, 340 [1942]; **42**, 228 [1946]). A methyl group which has been activated by neighboring double bonds loses a hydrogen atom, and a peroxide radical attaches to the free carbon radical. This hydroperoxide group in turn activates a neighboring ethylene space and so permits attachment of sulfite. I.D.C.

Tanning with Vegetable and Synthetic Tannins. I. The Influence of Acids and Salts on the pH Values of Tannin Solutions. H. Herfeld and K. Schmidt. *Das Leder*, **11**, 25–32 (1960).—Addition of salts to solutions of vegetable tan liquors raises the pH value. This influence holds for all tannin extracts regardless of tannin concentration. With salts of strong acids sulfate has a greater effect than chloride, and ammonium a greater effect than sodium salts. Salts of organic acids raise the pH more than those of mineral acids because of their alkaline reaction; the effect increases in the order: acetate, lactate, formate, oxalate. The salt effect remains during addition of acid so that the amount of acid needed to reach a given pH value increases proportionally as the amount of salt increases. In every acid-salt system the same pH value can be reached either with small amounts of acid and salt or with large amounts of each. In the latter case the anion will have a strong effect on the progress of tanning and on leather properties because of its buffering action, influence on diffusion, etc. The following table shows pH values of different tannin solutions containing 1 g. tannin per 100 ml. after addition of 10 milliequivalents (per g. tannin) of various neutral salts.

Extract	Salt and its equivalent weight							
	None	Sodium chloride 58.44	Ammonium chloride 53.50	Sodium sulfate 71.03	Ammonium sulfate 66.07	Sodium formate 68.02	Sodium lactate 112.08	Sodium acetate 82.06
Wattle	4.52	4.82	4.98	4.96	5.02	5.64	5.75	6.37
Quebracho	4.45	4.85	4.98	4.89	5.00	5.83	5.92	6.34
Quebracho, sulfited	6.15	6.57	6.64	6.59	6.64	6.69	6.74	6.98
Oak wood	3.62	3.88	3.97	3.94	4.02	4.87	5.02	5.70
Chestnut wood	3.10	3.37	3.49	3.50	3.62	4.79	4.96	5.69
Chestnut wood, sweetened	4.12	4.44	4.51	4.48	4.57	5.13	5.30	5.89
Myrobalans	3.20	3.39	3.51	3.48	3.60	4.50	4.64	5.31
Sumac	3.76	4.07	4.18	4.12	4.26	4.66	4.83	5.52

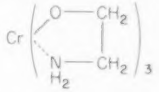
Curves and tables show pH values of wattle extract solutions after addition of different combinations of mineral and organic acids and their salts. Burton's method for total acid by titration to pH 6.5 or 5.8 (see *J.S.L.T.C.*, **35,** 170 [1951]) may give false results if larger amounts of salt are present. His method for salts of weak acids by titration to pH 2.0 may not always be applicable because in the presence of larger amounts of salts of strong acids the pH value may be below 2.0 without addition of hydrochloric acid even though weak acids are known to be present. Sodium chloride had little influence on results by this method, but sodium sulfate caused high values. **II. The Influence of Salts of Strong Mineral Acids on Tanning with Wattle Bark Extract.** *Ibid.*, 52–60.—The influence of varying amounts of salts of strong acids on the tanning action of wattle bark liquors were studied. Pieces of cattlehide were used for three series of tests of 24 tannages each. Tanning was started in liquors containing 5 g. tannin per l. and completed in 33 days in liquors containing 50 g. per l. Four salts were used, the chlorides and sulfates of sodium and ammonium. In the first and second series 0, 5, and 10 milliequivalents per g. tannin of the salts were used; and in one set of 12 the tan liquors were left at their natural pH, and in a second set of 12 they were adjusted to pH 3.5 with hydrochloric or sulfuric acid for series 1 and with acetic acid for series 2. In the third series the liquors contained 0%, 1%, or 5% of the salts on the liquor basis, and one set of 12 was acidified to pH 3.5 with acetic acid. The tan liquors were not strengthened, but new liquors were used for each higher tannin concentration in order to maintain the proper salt concentration. The tannages for series 3, in which the amount of salt was based on the liquor rather than the tannin, were started in much higher salt concentrations than those of series 1 and 2, but the tannages with 1% salt were completed at lower salt concentrations. The results showed that with salt present more acid could be put into a system at a given pH. With organic acid pH could be maintained at a constant value much more easily than with strong acids because of the reserve of undissociated organic acid. Salts repressed swelling so that if they were present the leather was softer and more flexible. Leather color was proportionally lighter the lower the pH of tanning and the more salt of a strong acid that was present. With increasing amounts of salt of a strong acid in the tan liquor diffusion of tannin into the hide

increased, especially if the salt was present in the first tanning stages and swelling was repressed. Salts, however, lowered the degree of tannage in all series, and this low degree of tannage was not overcome by increasing the time of tanning to two months. Salts of strong acids had no effect on tensile strength of the leather but increased stretch, especially if the tanning was in an acid medium and the salt was present in the initial stages. Increasing the salt content of the tan liquor caused increases in rate of wetting and water absorption of the leather. This effect was greater the greater the amount of salt, and it also was greater for leather tanned at pH 3.5 then for that tanned at the natural pH. To achieve rapid tanning and leather of best quality, large amounts of salts of strong acids in the tan liquors should be avoided. If such salts are used to repress swelling, they should be used only in the initial tanning stages or in the pickle. Syntans or modified vegetable tannin extracts should not have a high salt content, especially not of ammonium salts. I.D.C.

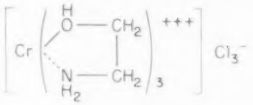
The Solution-Stability of Anionic Emulsifiers in Chrome Tan Liquors. D. Post. *Das Leder*, **11**, 32–38 (1960).—Fatliquor emulsions are desired that are stable in chrome tan liquors. These are mainly cationic or nonionic, but anionic fatliquors are known such as the sulfo acids of oxidized train oil that are formed by treating highly unsaturated train oils with bisulfite in a current of air. Alkylsulfates are good emulsifiers and are quite soluble. Although they are saponified by acid, they are preferable to alkylsulfonates which, while they do not saponify, are not very soluble. Alkylsulfates react electrovalently with chromium salts but do not enter the coordinate sphere, for there is no color change. There is maximum precipitation when the charges are equal. One mole of hexaquochromic chloride $(Cr(H_2O)_6)^{+++}Cl_3$ is precipitated completely by 3 moles of alkylsulfate $(R\text{-}OSO_3^-)$; but dichlorotetraaquochromic chloride $(CrCl_2(H_2O)_4)^+Cl$, by one mole. If an excess of alkylsulfate is added, the precipitate redissolves. This precipitate of chromic chloride and anionic emulsifier is slightly absorbed by apolar solvents such as petroleum ether or carbon tetrachloride and collects at the water-solvent interface. As polarity of the solvent increases solubility of the precipitate increases until with such solvents as alcohols, acetone, dioxane, etc., there is complete solution and only one phase. Ether and ethyl acetate form an intensely colored third phase between the water and solvent layers. Introduction of hydrophylic groups in the emulsifier molecule increased stability of chrome salts. The best stability was with an alkylsulfate in which two ether oxygen linkages had been built into the chain. Imino groups (-NH-) were also good, but these compounds are essentially cationic. Peptide groups (-CONH-) can be incorporated into emulsifiers by treating fatty acids with aminoalcohols and sulfuric acid to form products of the Igepon C type. The precipitates which Igepons form with chrome salts are not voluminous and dissolve in only a small excess of emulsifier. With 30% basic chromium sulfate solution a small precipitate formed with ethylene Igepon (1.8 mole per mole Cr); the solution become cloudy with propylene Igepon, but with butylene Igepon it remained clear. The anion also influenced stability. Replacing chloride by sulfate reduced the amount of emulsifier required to redissolve the precipitate, because sulfate entered the chromium complex and so reduced its charge. Hexaquochromic chloride, sodium dodecylsulfate (DDS), and ether formed three layers, but if sodium sulfate was added and the mixture was shaken, the middle layer vanished. Basicity of the chrome salt played an important role. Aged chromic chloride

solutions ranging in basicity from 0% to 75% were treated with from 1 to 6 moles of DDS per mole of Cr and shaken with an excess of ether. At basicities of from 20% to 50% the middle ether layer separated into two phases, the lower of which was more strongly colored by chrome. Apparently chromium salts of different basicities and therefore different degrees of aggregation were present in the middle layers. In the water layer the least color was found with 3 moles of DDS per mole of Cr at basicities from 0% to 20%, with 2 moles at basicities from 30% to 64%, and with 1 mole at 75% basicity. The ether layer was colorless at basicities below 50%, then developed a green color which increased in intensity as basicity increased. Preparation of the emulsifying agents is given. I.D.C.

Tanning with Ethanolamine Complexes of Chromium. A. Küntzel and H. Trabitzsch. *Das Leder*, **11**, 49–51 (1960).—Preparation of a monoethanolamine chelate complex of chromium has been described (see *JALCA*, **54**, 702 [1959]). This compound, which has the structure



has no charge and therefore is insoluble in water. It readily dissolves in hydrochloric acid solution with the addition of three equivalents of acid to form



The chelate character, however, is lost and water attaches to the bonds that are set free to form $(H_2O)_3Cr(H_2NCH_2CH_2OH)_3Cl_3$. This tris-aminoethanol-triaquochromium chloride decomposes slowly, and the ethanolamine that is set free then gradually increases the basicity of the zero basic chromium chloride by combining with the chloride ion. A tanning agent is thus available that can be used on unpickled stock because at the start it is 0% basic. During tanning, the basicity slowly increases, and conditions can be adjusted so that the leather does not need neutralization. Three equivalents of acid were required to produce full, flexible leather, and there appeared to be a slight advantage in adding the acid in three portions at two-hour intervals during the 24-hour tannage. The high price of monoethanolamine will prevent commercial use of the process. Di- and tri-ethanolamine complexes do not tan well; these complexes may be too stable. I.D.C.

Quality of Austrian Leathers, Raw Materials, Tanning Extracts, and Allied Products. J. A. Sagoschen. *Leder Kurier*, **4**, 68–77 (1960).—An address discussing present quality of leathers and products used in tanneries. Sole leather has improved in all respects except water resistance, which is poorer. Analytical values, in general, show improvement. Averages are well within the limits for leathers required to meet specifications. Military lining and also shoe upper leathers may require very strict sweat-resistance specifications because of the use of rubber soles. I.D.C.

H. Nursten. **Recent Progress in the Field of Dyestuffs for Leather.** *J. Soc. Leather Trades Chemists*, **44**, 182–91 (1960).—Utilizing a background of information from the second edition of the *Color Index*, the author considers recent advances in dyestuff chemistry under the headings: anionic dyes, after-treatments, metal-complex acid dyes, reactive dyes, and the remaining types. J.M.C.

The Mechanical Properties of Collagen Fibers: Stress-Strain Curves. F. Morgan. *J. Soc. Leather Trades Chemists*, **44**, 170–82 (1960).—Stress-strain curves obtained for untanned, vegetable-tanned, and chrome-tanned collagen fibers under various test conditions are discussed. Fibers were tested at 0, 33, 66, and 100% R. H. In general, the shape of the stress-strain curve was similar for tanned and untanned fibers, and widely different test conditions did not significantly alter the shape of the curves. All fibers were more easily extended in high humidities than at low. The stress-strain behavior is adequately described by the equation $E = aP^n$ where E and P are extension and load respectively, a and n being constants determined by the kind of fiber and test condition. The direction of the deviation of the collagen curve from linearity (a bending toward the load axis as the stress is increased) is characteristic of fibers with a spiral molecular structure. The stuctural unit controlling the stress-strain behavior of collagen is the filament or the larger protofibrils. J.M.C.

Determination of Stiffness of Soling and Insoling Materials. A. Horsfield. *J. Soc. Leather Trades Chemists*, **44**, 191–201 (1960).—Specimens are bent symmetrically about their midpoint by applying known weights to a pan serving as one side of a confining chamber. The displacement of the pan per weight applied provides stiffness data. The importance of preflexing the specimens is stressed. J.M.C.

Effect of Various Masking Agents in Chrome Tanning. Y. Oono and Y. Fukui. *Bull. Japanese Assoc. Leather Technol.*, **6**, 15–22 (1960) (English summary).—Cr liquors were treated with from 0.5 to 5.0 equivalents of masking agent (Na salts) per Cr, and changes of pH value and tanning power with time of aging were studied. As a result of these studies, masking agents were divided into 2 groups: (1) those that increase the astringency of the Cr liquor (Na_2SO_3, $NaNO_2$, Na succinate, adipate, and phthalate) and (2) those with strong penetrating power (Na formate, acetate, tartrate, citrate, and oxalate). Those in the first group increase the Cr content of leather and become more reactive on aging. pH value decreases continuously on aging. Titration curves change little. The tanning power of liquors in the second group decreases on aging as the stability of the Cr complexes increases. pH values first decrease and later increase on aging. H.B.M.

Studies on Vegetable Tanning. VI. The Fixation of Chrome Complexes to Vegetable-tanned Hide Pieces. Y. Inouye, H. Okamura, and Y. Iizuka. *Bull. Japanese Assoc. Leather Technol.*, **6**, 1–7 (1960) (English summary).—Hide pieces were tanned with chestnut, wattle, myrobalans, sulfited quebracho, and tannic acid, and retanned with Cr complexes ranging from Cr^{3+}

to Cr^{3}. Fixation of Cr depended on degree of vegetable tannage, kind of tannin, pH or Cr liquors, a charge on Cr complex. A high degree of vegetable tannage resulted in lowered Cr fixation from both cationic and anionic Cr compounds. H.B.M.

Supercontraction of Wool Fibers and Creep in the Postyield Region. K. J. Whiteley. *Nature*, **186**, 473 (1960).—From studies of supercontraction of wool fibers in 1*N* HCl containing 4*M* NaCl, it was concluded that the process took place in 2 phases corresponding to areas of "strong" and "weak" hydrogen bonding lying in series along the microfibrils. The "strong" hydrogen bonds responsible for the later phases of supercontraction may also account for a major part of the technologically significant variations in the creep properties of wool fibers. C.L.D.

Correlation of Instron and Elmendorf Tearing Strength Results. J. F. Krasny and D. C. Borton. *Textile Research J.*, **30**, 400–1 (1960).—The correlation between the Instron and Elmendorf methods of tearing strength testing was investigated for a group of fabrics covering a rather broad range of weights, weaves, finishes, component fiber types, and testing conditions. In lower tearing strength regions the Elmendorf results correlated well with the Instron tongue tear results; at higher tearing strength levels a distinct effect of weave appeared, with an opener weave rating relatively high and a somewhat tighter weave relatively low on the Elmendorf scale. C.L.D.

Compressional Behavior of Textile Fibers. J. B. Miles. *Textile Research J.*, **30**, 408–9 (1960).—Stress-strain and elastic recovery curves of oriented nylon bristle in tension and compression were determined. The striking differences between the tensile and compressive behavior of oriented nylon indicate that the bending behavior of oriented fibers in general may not be predictable from measurements of the tensile behavior alone. C.L.D.

Compressional Behavior of Textile Fibers. S. Backer. *Textile Research J.*, **30**, 405–7 (1960).—Compressive stress-strain curves of nylon, polyethylene, and saran monofilaments are presented, and a discussion is given of their importance in usages involving fiber axial compression. C.L.D.

Occurrence of a Nonfibrillar Elastin in the Earthworm. P. Van Gansen-Semal. *Nature*, **186**, 654–55 (1960).—Histochemical and physical evidence and amino acid composition support the view that the cuticle of the earthworm gizzard is a nonfibrillar elastin. C.L.D.

Amino Acid Composition of Proteins from Surface Tissue of the Tongue. C. J. Barnes and L. N. Ferguson. *Nature*, **186**, 617–19 (1960).—Proteins of the mucous membrane and papillae from human tongue contain 7.3% hydroxyproline. Tongue-surface proteins, however, differ from collagen in that the former contain tryptophan, a much smaller percentage of proline and glycine, and a higher amount of lysine. C.L.D.

The Tropocollagen Macromolecule and its Properties of Ordered Interaction. F. Schmitt and A. Hodge. *J. Soc. Leather Trades Chemists*, **44**, 217–46 (1960).—This is a very thorough review of the most recent advances in the state of knowledge of the fundamental chemistry of collagen. Based on detailed examination of the various ordered aggregation states of the tropocollagen molecule in the electron microscope and, in particular, the examination of the so-called segment long-spacing form (SLS) which the authors consider a "molecular fingerprint" which indicates polar side-chain distribution, a mechanism is formulated for the end-to-end linkage of the macromolecules, a process presumably involved in fibrogenesis *in vivo*. The effect of treatment with trypsin, or pepsin, or by mild sonic irradiation on the end-to-end polymerization is discussed. The trypsin treatment is shown to split off an acid peptide (or peptides) containing tyrosine but no basic groups. J.M.C.

Microelectrophoretic Studies of Soluble Collagen. I. Gilbert. *Biochimica et Biophysica Acta*. **40**, No. 1, 156–62 (1960).—A microelectrophoresis unit is used to determine mobilities of soluble collagen adsorbed on small paraffin droplets. Mobilities are measured at collagen concentrations assuring surface saturation of the oil droplets. A typical flat isoelectric zone, pH 7–8.5, was observed; the result was in good agreement with similar measurements on insoluble collagen. Citrate ions are shown to influence significantly the mobility. J.M.C.

Migration of Liquids and Materials Dissolved in Them in Leather. R. G. Mitton. *Das Leder*, **11**, 118–29 (1960).—Migration of water and various solutions was studied by building up columns of about 160 disks of well-washed Cr-vegetable-retan leather. In measuring rates of diffusion, the lower 148 disks were brought to a uniform, high water-content, or contained a solution of NaCl, tannin, etc., while the upper 12 disks contained water at a uniform lower concentration, not necessarily bone-dry. The column was enclosed in a glass tube, closed at the bottom, under light pressure. Migration of water, salt, etc., was measured by analyzing the separate disks after a period that was so short that the "flow wave" did not reach to the bottom of the column. Mitton showed (abstr. *JALCA*. **51**, 198 [1956]) that migration of water in leather takes place almost entirely through the capillaries. It can be treated mathematically like a diffusion process. The diffusion coefficient, D, can be calculated from the equation:

$$D_{C_1} = \tfrac{1}{2} t \, dx/dC \cdot \int_0^{C_1} x \, dC$$

where C=g. H_2O/cm.^{3}, t=time, x=serial no. of disk above the boundary, and dx/dC and the integral can be evaluated graphically from a curve obtained by plotting C against the serial no. of the disk. For $C<0.2$ g/cm.^{3}, H_2O migrates by vapor diffusion, and D was found to decrease with increasing C. At higher values of C, capillary transport of liquid H_2O occurs, and D increased rapidly with C. When the lower column was impregnated with a strong, viscous solution of sorbitol or myrobalans extract, it was expected that D would be reduced because of the viscosity. Actually, if the upper column contained less than 0.21 g. H_2O/cm.^{3}, no migration of the solution into the upper column

took place, because the solution could not wet the dry leather fiber. When the upper column contained more water, migration occurred, but very slowly. It is shown that when leather contains more-or-less pure water, D is large enough so that the water content of the leather remains uniform throughout its thickness during most of the drying period, but if the leather contains a viscous solution, tan liquor for example, then D is so low that the surface layers contain less water than the interior right from the start. Diffusion of NaCl was studied by impregnating the lower column with a NaCl solution and the upper column with various concentrations of H_2O. NaCl was determined in the individual disks after a limited diffusion period. No diffusion of NaCl occurred if the upper column contained less than 0.14 g. $H_2O/cm.^3$, supposedly because of absence of a liquid phase. At higher water-contents, D for NaCl increased rapidly with water content, reaching a limit in H_2O-saturated leather that was about ¼ the diffusion constant for NaCl in free solution. This is expected because the capillaries are so tortuous, and because half the apparent volume is occupied by leather fibers. Migration of salt and tannin during drying was studied by setting up short columns of disks, originally uniform through their lengths with respect to water and solute, and allowing evaporation to take place from the top disk until drying was more or less complete. The disks were analyzed after various periods. On drying the leather containing salt solution at 50°C. for 163 hr., it was found that the water content remained almost uniform throughout the column so long as the evaporation surface coincided with the top of the column, but accumulation of NaCl in the upper disks was observed from the outset, increasing until the water content had dropped to about 50% of the dry leather weight, when diffusion of salt stopped. When columns were dried very slowly, at 21°C. and 70% relative humidity, less salt accumulated in the surface layers because time was afforded for back diffusion. In similar experiments employing strong tannin solutions the water contents of the upper disks declined, and their tannin contents increased, right from the start. The behavior of solutions of paraffin in various organic solvents was practically like that of NaCl solutions. When the upper disks were treated with sulfated oil, or mixtures of sulfated and mineral oil, the peak accumulation of NaCl during evaporation was displaced to the topmost nonoiled disk, provided that the oiled disks contained not less than 12% added oil. While oiling retards evaporation, this is not enough to explain the effect on salt deposition, and it is suggested that concentrated salt solution cannot wet the fibers of the oiled leather. H.B.M.

The Effect of Salts of Organic Acids on Tannage with Wattle Extract. H. Herfeld and K. Schmidt, *Das Leder*, **11**, 105–10 (1960).—Dehaired, delimed steerhide samples, split to uniform thickness, were tanned for 2 months in wattle extract liquors in which the tannin content was increased progressively from 0.5% to 5.0%. Tannages were carried out with addition of 4 salts (Na acetate, formate, lactate, and oxalate), each at 3 concentrations (0.0, 0.1, and 0.5 V) and at 3 pH values for each concentration (unadjusted, adjusted to pH 4.5 with the corresponding organic acid, and adjusted to pH 3.5 with HCl), making a total of 36 tannages. Penetration was followed by periodic measurement of the thickness of the tanned layers, and the degree of tannage was determined by analyzing the leathers after 26 days and after 2 months. The liquors were changed completely each time the tannin concentration was stepped up, and the same salt concentration and pH value were used through-

out the whole tannage. The salts alone raised the pH values, in increasing order: oxalate, formate, lactate, and acetate. Presence of the salts minimized changes in pH while the liquors were in contact with the skin, due to buffering action. The salts lightened the color of the leathers tanned at pH 3.5, in increasing order: acetate, lactate, formate, and oxalate. Acetate darkened the leather tanned at pH 4.5, and all the salts except oxalate darkened the leathers tanned at the unadjusted (high) pH values. At each pH value, the rate of penetration increased with salt concentration, but the degree of tannage decreased, even after 2 months' tannage, except that leathers tanned in 0.1*N* salt at pH 3.5 showed slightly increased degree of tannage. Presence of salts during tannage increased the flexibility, stretchiness, and water absorbency of the leathers. If these salts are added at all, it should be only during the early stages of tanning, to speed up penetration and produce flexible leather.

H.B.M.

A Study of the Precipitation of Vegetable Tannins by Formaldehyde and Urea. R. Lasserre. *Bull. Assoc. Franc. Chim. Ind. Cuir.* **21,** 148–61 (1959).—Tannin solutions of 20% extracts of sulfited quebracho, ordinary chestnut, and sweetened chestnut were reacted with increasing amounts of formaldehyde and urea, at pH values under 4.0. The solutions were evaporated in air for 8 days in crystallizing dishes at ambient temperature, and the residues were dried in air, weighed, and their appearance noted. The results indicated an increase of insoluble material with an increase in urea-formaldehyde. With quebracho the insoluble material formed was less than that obtained with the chestnut extracts and also less than the residue of the urea-formaldehyde solution alone.

The tannin solutions were also reacted with increasing amounts of formaldehyde alone under identical conditions. After evaporation of the solution and drying of the residue, the insolubles obtained increased slightly with an increase in formaldehyde.

It was found that ½ hour after the preparation of the formaldehyde-urea mixture, 77% of the formaldehyde was in a free state, and after 1 hour the amount found in a free state was 64%. The action of free formaldehyde on the tannins produces a decrease in the formation of urea-formaldehyde tannin resins. It is believed that when the urea-formaldehyde is put in contact with a vegetable-tanned leather, the free formaldehyde reacts with the tannins present in the top layers of the leather, thereby reducing the formation of urea-formaldehyde tannin resins. The nontannins did not give insoluble combination products with the urea-formaldehyde solutions.

Shavings of chestnut-tanned leather were agitated with 3.5 c.c. of urea-formaldehyde solution containing 4% urea at pH values of 8, 5, and 3.5. After agitation for 8 hours all the experiments were left for 2 days in solution before drying. The water-soluble materials were then determined on the leather shavings. The results showed very little difference in the amount of water solubles for the different experiments. The effect of the initial acidity was slight, since neutralization occurred in the leather. Most of the urea was found in the soluble matter at a pH of 4.7 (final).

However, the addition of oxalic acid in sufficient quantity to obtain a final pH of about 3.5 caused an increase in insolubilized urea. The insolubilized urea was 64.3% in one experiment and 81.5% in another. Acidity appears

to be a major factor regulating the highly complex reactions which are produced in the leather in the insolubilization of the tannins by the urea-formaldehyde. R.L.H.

Weathering and the Resulting Chemical Changes in Some South African Merino Wools. D. F. Louw. *Textile Research J.*, **30**, 462–67 (1960).—Weathering of wool on the sheep's back results in destruction of cystine and formation of cysteic acid. This rupturing of covalent disulfide linkages of cystine leads to increased dye absorption and higher alkali solubility of weathered tips of wool in comparison with the root section. Weathering destroys about 20% of the tryptophan present in wool and increases the α-amino content by about 50%, probably due to peptide hydrolysis. Weathered wools show a 20% increase in glycine content and a decrease of 10% in threonine. C.L.D.

Electrical Conduction in Keratin. J. E. Algie, J. G. Downes, and B. H. Mackay. *Textile Research J.*, **30**, 1432–34 (1960).—The increase in electrical conductivity of keratin fibers after the application of an abrupt change of the relative humidity from 0% to 90% was examined as a function of time. It is suggested on the basis of the data that the wool-water system is a protonic semiconductor and that a hydrogen-bonded network must be formed before conduction can take place. C.L.D.

Biological Significance of a Peptide Containing Hydroxyproline During the Development of *Carrageenin Granuloma*. M. Chvapil and B. Cmuchalová. *Nature*, **186**, 806–7 (1960).—Granuloma tissue from guinea pigs contained a peptide of hydroxyproline which formed 20% to 65% of the total filtrable tissue hydroxyproline in the first days of granuloma development. This percentage gradually decreased. It is suggested that the accumulation of peptides containing hydroxyproline is connected with early collagen synthesis. C.L.D.

Isolation of Antibodies to Gelatin from Antigen-Antibody Complex by Proteolysis. R. Arnon and M. Sela. *Science*, **132**, 86–87 (1960).—Rabbit antiserum to gelatin was prepared, and the antibodies were precipitated with gelatin. When the gelatin-antigelatin complex was treated with collagenase and the gelatin fragments were removed by dialysis, pure antibody, which could be again precipitated with gelatin, was isolated. Antibodies to tyrosylgelatin were similarly prepared. When the tyrosylgelatin-antityrosylgelatin complex was treated with collagenase, peptides containing the active antigenic sites remained bound to the antibody; the pure antibody could therefore not be recovered. C.L.D.

Zinc Sulfate Treatment of Parakeratosis in Cattle. S. P. Legg and L. Sears. *Nature*, **186**, 1061–62 (1960).—Cattle grazing in British Guiana on soils that produced grasses of low Zn content developed parakeratosis; in acute

cases over 40% of the body surface was affected. Calves from such cows shed the bulk of the hair from large areas and showed hyperkeratinization along the mid-line of the back. The hair and skin of such cattle rapidly returned to normal after oral administration of $ZnSO_4$. C.L.D.

Investigations on the Penetration of Concentrated Vegetable Tannin Solutions into Hide. E. Heidemann. *Das Leder*, **11**, 99–105 (1960).—The penetration of strong tan liquors into hide (not pretanned) has heretofore received little study. The rate of penetration from dilute liquors is governed chiefly by affinity of the tannin for hide, but in concentrated liquors it depends mostly on viscosity and on osmotic forces. Pieces of hide were immersed in wattle and chestnut solutions, from 2° to 25°Bé., at 20° and 37°C., and the rate of penetration was determined by measuring the widths of the tanned layers at daily intervals. The rate of penetration increases with concentration to a certain optimum concentration, and thereafter decreases. At very high concentration, penetration stops altogether after 1 or 2 days, resulting in the well-known casehardening. This has generally been attributed to blockage of the interfibrillary spaces of the surface layers by large tannin particles, but H. believes it to be due to shrinkage of the interfibrillary spaces in the untanned layer because of osmotic dehydration. The fact that casehardening seldom or never occurs when hide is lightly prechromed casts doubt on the usual explanation. Analyses of the untanned layers show that the water content declines progressively with time and with increasing tannin concentration, dropping from about 67% to about 51% in extreme cases. Similar dehydration takes place in concentrated sugar solutions, and the penetration of the sugar also comes to a stop. Gelatin cubes are visibly shrunken in strong tannin solutions. The critical concentration depends on viscosity and particle size as well as on the extent of osmotic dehydration. The optimum concentration is much affected by viscosity. The optimum concentration for wattle is lower than for chestnut because the former has a higher viscosity, and the optimum for chestnut is the same at 20° and 37°C. because its viscosity changes little with temperature, while the optimum for wattle increases with temperature because of a marked drop in viscosity. The viscosities of wattle and chestnut solutions increase by about 20% in going from pH 2 to 5. When strong tannin solutions are incubated at 100°C. for 1 to 28 days, the viscosity (at 25°C.) first declines slightly and then increases sharply, probably because of polymerization. The results obtained with wattle and chestnut are shown to hold for several other tannins. H.B.M.

The Mechanism of Salt Stippen Formation and Suggested Methods of Control. J. J. Tancous and F. O'Flaherty. *Das Leder*, **11**, 129–35 (1960). —German translation of *JALCA*, **55**, 66–78 (1960). **Remarks on the Foregoing Investigations of J. J. Tancous and F. O'Flaherty, "The Mechanism of Salt Stippen Formation and Suggested Methods of Control".** A. Küntzel. *Ibid.*, 135–39 (1960).—Bergmann's theory that salt stippen, which he renamed "fungus stippen", are caused by fungus infection of the living hide has been widely accepted because of the high repute in which its author is held. Bergmann and his associates tended to ascribe all skin defects, great and small, to biological causes. They thought that the white, formless material enclosed in the stippen was a keratinous growth produced in the living hide as a reaction to the fungus infection. A critical study of Bergmann's publica-

tions leads to the conclusion that the "hair fungus" theory is "an astonishing feat of the imagination", in which the fundamental fact of the inorganic nature of the material included in the stippen is carelessly passed over without experimental investigation. X-ray diagrams have confirmed that the stippen in unwashed skin contain $MgNH_4PO_4 \cdot 6H_2O$, as postulated by Tancous and O'Flaherty from chemical evidence. The relationship between various types of salt damage and impurities in the salt demands much more study. It is certain, however, that the "fungus stippen" theory must be abandoned, because that theory works against an intelligent fight against this type of skin and leather damage. H.B.M.

The Origin of the Crossband Pattern in Collagen. K. Kühn. *Das Leder*, **11**, 110–17 (1960).—An address. In addition to findings previously reported (see abstr., *JALCA*, **54**, 369 [1959]), investigations on crossbanding of long spacing segments are described (see Schmitt, Gross, and Highberger, abstr., *JALCA*, **52**, 167 [1957]). This material, with a period of 2800 A., yielded at least 35 bands when treated with HCHO, followed by phosphotungstic acid, sulfitochromium complexes, or uranyl acetate. As in the case of native collagen, these reagents enhanced the intensities of different bands. A composite photometric absorption curve was obtained by superposing curves that were displaced by ¼, ½, and ¾ of the long period length, onto the photometric curve of the electron microscope photograph of long-spacing collagen treated with uranyl acetate. This composite curve closely resembled the photometric absorption curve of a similar preparation of native collagen, which supports the idea that the usual 600–700 A. period results from aggregation of tropocollagen fibrils linearly displaced with respect to each other by ¼ of the long period. H.B.M.

Comparative Biochemistry of Hides and Skins Collected from Different Regions. I. Distribution of Certain Amino Acids, Carbohydrate Constituents and Lipids in Hides and Skins of U.P. and Hyderabad Regions. K. Thomas Joseph, S. M. Bose, and Y. Nayudamma. *Bull. Central Leather Research Inst. Madras*, **6**, 465–77 (1960).—Samples were taken from numerous dry-salted skins, including buffalo, cow, goat, and sheep, some slaughtered and some fallen, some from healthy and some from diseased animals. The specimens were soaked, fleshed, shaved to remove hair, and hydrolyzed with 0.1*N* HCl and Amberlite IR-120(H). The hydrolyzate was analyzed for hydroxyproline, proline, glycine, tyrosine, tryptophane, reducing sugars, and hexosamine. Separate skin samples were analyzed for fats. Hydroxyproline was lower for skins of diseased and fallen animals, while carbohydrate constituents, tyrosine, and tryptophane were higher. For the different species, hydroxyproline declined in the order: buffalo, cow, goat, sheep. There was no connection between hydroxyproline content and shrink temperature of cow and buffalo hides. The lower hydroxyproline and higher tyrosine and tryptophane contents probably reflect variations in the ratio of collagen to other skin proteins. Fat tended to be lower in skins of diseased animals. H.B.M.

Determination of the Protein Content of Pickling Liquors in Leather Manufacture. J. Inczédy. *Bőr- és Cipőtechnika*, **9**, 57–60 (1959); *Hung. Tech. Abstr.*, **12**, 20 (1960).—For a routine analysis of the protein content of pickling solutions, the samples may be purified from suspended impurities by filtration through a *G2* sintered glass filter. If the protein nitrogen present is 1 to 2 g. per liter, the determination may be carried out very quickly from 20 ml. of filtered solution after the addition of HCHO by titrating with 0.1*N* NaOH solution in the presence of phenolphthalein indicator. The Loiseleur-Thillard method is also suitable for the determination. After the addition of a mixture of alcohol and ethylene glycol, the sample may be titrated by 0.1*N* alkali solution and then with 1*N* HCl in the presence of phenolphthalein or methyl orange indicator. More accurate results are obtained by the former method. With nitrogen contents of 0.1 to 0.5 g. per l. the protein content may be measured by a quick photometric method employing phenol reagent (phosphotungstic-phosphomolybdic acid lithium salt). The protein nitrogen is calculated from the value of extinction at 570 mμ by the aid of a calibration curve. The above rapid procedures may be checked by the Kieldahl method. H.B.M.

The Effect of Rolling and Washing. G. Tóth. *Bőr- és Cipőtechnika*, **9**, 75–77 (1959); *Hung. Tech. Abstr.*, **12**, 20 (1960).—The work of wear can be determined with a 3% standard deviation on the new wear test machine. The specific work of wear is slightly raised by rolling which can be deduced from the increase in specific gravity. At low pressures the difference is negligible; it is significant however at high pressures. On removal of the material that can be washed out, the work of wear referred to the weight of the fibers measured previous to washing reduces as well. H.B.M.

Dynamic Fatigue Tests on Belt Leathers. G. Tóth. *Bőr- és Cipőtechnika*, **9**, 50–53 (1959); *Hung. Tech. Abstr.* **12**, 20 (1960).—Leathers can be broken by stresses considerably below their tensile strength when subjected to continuous loading. The crackling noise produced by the breakage of the bundles of fibers can be observed with an amplifier when stresses of 40% of the tensile strength are applied. Thus the tensile strength of leather can be estimated with an accuracy of 10–15% in a nondestructive manner. The leather will break much sooner when loaded dynamically than with continuous loading and the curve of durability will also be steeper. The dynamic fatigue testing machine described in the article can also be applied for establishing technological changes. H.B.M.

The Roles of Prolyl Residues in Polypeptide Monolayers. III. Surface Films of Gelatin. S. Ikeda and T. Isemura. *Bull. Chem. Soc. Japan*, **33**, 137–40 (1960).—The properties of gelatin films on salt-free and *M* KCl solutions at 3 different pH values support the conclusion that gelatin contains numerous L-prolyl-L-hydroxyprolyl bonds. These properties can be explained by assuming that parts of *cis*-L-prolyl-L-hydroxyprolyl bonds form the film, and parts of *trans*-L-prolyl-L-hydroxyprolyl bonds dissolve in the aqueous subphase. H.B.M.

Effect of Neutral Salts on the Chrome Complex in Chrome Liquors Used for Tanning. D. Ramaswamy and Y. Nayudamma. *Bull. Central Leather Research Inst. Madras*, **6**, 429–34 (1960).—NaCl or Na_2SO_4 was added to solutions of Cr alum or $Cr(ClO_4)_3$, generally 33% basic, and absorption at 220 and 230 mμ was measured at intervals for 24–48 hr. In most cases, absorption increased during the first hour and thereafter remained practically constant. The rapidity with which equilibrium is attained indicates that "outer shell" or ion pair complexes are formed, rather than "inner shell" or coordination complexes, since the latter generally are formed rather slowly.
H.B.M.

Investigations on the Curing of Hides and Skins. IV. S. C. Nandy, S. N. Sen and K. T. Sarkar. *Bull. Central Leather Research Inst. Madras*, **6**, 413–28 (1960).—Four lots containing 6 large calfskins each were cured as follows: (1) green-salted with 35% solar salt; (2) brined in saturated salt, drained and lightly resalted; (3) brined, drained, brushed on flesh side with 0.2% Na pentachlorophenate dissolved in brine, and lightly resalted; (4) washed, drained, brushed on flesh side with 0.325% Na pentachlorophenate dissolved in water, and then green-salted with 15% solar salt. All the skins were cut into sides, and half the sides in each lot were fleshed before curing. After 7½ months' storage at 15°C., Lots 1 and 2 showed much red heat and hair slip, while the lots cured with antiseptic were practically free from these damages. There was no significant difference between green-salted and brined skins, or between prefleshed and nonfleshed sides, but subsidiary laboratory tests showed that brine cure proceeds much faster for prefleshed sides. The sides were processed for Cr upper leather. Leather weight yields, on green weight, increased very slightly in the order, Lots 1 and 2, Lot 3, Lot 4, but area yield per lb. green weight increased in the reverse order. No significant differences in yield or in leather quality were noted between prefleshed and nonfleshed sides.
H.B.M.

A Study of the Chemical Shrinkage and Relaxation of Collagen Fibers. M. Chvapil and R. Zahradnik. *Biochim. Biophys. Acta*, **40**, 329–39 (1960).—The kinetics of the course of shrinkage and relaxation of collagen fibers (rat-tail tendon fibers of approx. 0.15 mm diameter) is described. Data were obtained by following changes in fiber length and by determining the concentration of liberated substances (mucoproteins) on immersing collagen fibers in $NaClO_4$ solution. Iodide, perchlorate, thiocyanate and xanthogenate are anions most effective in promoting shrinkage and relaxation of collagen fibers. Shrinkage in $NaClO_4$ solution over a temperature range 16°–30° involved an energy of activation of approximately 55 kcal. mol^{-1} while for relaxation in the same medium a value of 9.6 was determined. Shrinkage is connected with splitting off of a mucoprotein and relaxation is due to rupture of the linkage between procollagen and metacollagen.
J.M.C.

The Formation of Fibrils from Collagen Solutions. 1. The Effect of Experimental Conditions: Kinetic and Electron-Microscope Studies. G. Wood and M. Keech. *Biochem. J.*, **75**, 588–98 (1960).—Measurement of the increased opacity of collagen (calf skin) buffer systems was employed in a study of the effect of experimental conditions (pH, ionic strength, tempera-

ture and collagen concentration) on the rate of fibril formation. Parallel to the rate studies, the morphology of the collagen precipitates was investigated by electron microscopy. The variation of fibril width with various experimental conditions is discussed and it is indicated that the ultimate fibril width is decided before any appreciable precipitation has occurred. Variation of rate of precipitation with ionic strength and pH indicates that it is controlled by electrostatic interaction between the soluble collagen particles. J.M.C.

The Formation of Fibrils from Collagen Solutions. 2. A Mechanism of Collagen-Fibril Formation. G. Wood. *Biochem. J.*, **75,** 598–605 (1960).—Fibril formation is regarded as the result of two processes: (a) nucleation, and (b) growth of the nuclei into fibrils by accretion of further soluble collagen particles. The reaction of the soluble particles with the surface of the growing fibrils is assumed to control the rate of growth. Equations are derived which qualitatively account for the occurrence of a lag period in precipitation and for the observation that the final distribution of fibril width is determined during the lag period. J.M.C.

The Formation of Fibrils from Collagen Solutions. 3. Effect of Chondroitin Sulfate and Some Other Naturally Occurring Polyanions on the Rate of Formation. G. Wood. *Biochem. J.*, **75,** 605–12 (1960).—Low concentrations of heparin and desoxyribonucleic acid were found to retard fibril formation while chondroitin sulfate A and C accelerated fibril precipitation. Chondroitin sulfate B and hyaluronic acid had no effect. Chondroitin sulfate A accelerates precipitation by affecting the nucleation process, the first step in fibril formation. Addition of chondroitin sulfate to collagen solutions pretreated with phosphate buffer at 0°C. retarded subsequent precipitation at 25°C., an indication that nucleation had occurred during pre-treatment and that the observed retardation was due to the effect of chondroitin sulfate A on growth. J.M.C.

The Physical Measurement of Color. A. Derbyshire. *J. Soc. Leather Trades Chemists*, **44,** 286–301 (1960).—The paper outlines the physical facts of color perception and shows how the C.I.E. system of color specification takes account of these facts and permits specification of color or color difference by three numbers measurable by methods which are described. The potential value of such measurements to industrial users of color is discussed and is illustrated by an outline of recent experimental work on color standardization and color match prediction. J.M.C.

Some Present-Day Requirements of Shoe Manufacturers and Wearers for Insole and Upper Leathers. L. Huggett. *J. Soc. Leather Trades Chemists*, **44,** 271–86 (1960).—The desirable properties of insole and upper leathers are discussed from the consumer's and the manufacturer's point of view, and these are related to the various chemical and physical tests performed at S.A.T.R.A. J.M.C.

The Manufacture of Pig Glove Leather. F. Stather, H. Herfeld, H. Moser, and K. Härtewig. *Ges. Abhandl. deut. Lederinst. Freiberg/Sa.*, **No. 14,** 87–102 (1959).—The successive steps in the process were critically examined

with respect to their contribution to production of stretchy, non-rubbery leather. Pig necks for gloves must be separated from the croupons intended for shoe leather before reliming, not after tanning, as the desired properties cannot be achieved merely by fatliquoring and mechanical treatment. The following treatments are necessary or desirable: partial degreasing after fleshing, using warm water and 0.5% NaOH; bristle destruction by drumming with Na_2S (painting offers no advantages); a 14-day reliming at about 25°C. using up to 10% lime in a liquor containing 50% old lime liquor; complete deliming; thorough degreasing; bating 5–8 hr. at 32°C.; pickling overnight with 1% H_2SO_4 and horsing 4 days out of pickle; a slow, scant tannage, starting with 0–10% basic Cr alum, followed by 42% basic Cr alum, both fed in many parts, with eventual neutralization to a shrink temp. of only 80°–85°C.; complete neutralization after splitting and shaving; light retannage with a replacement syntan; thorough fatliquoring; drying at room temperature; crusting; rewetting and dyeing; drying at room temperature; and second crusting. Hand beaming twice a week, or working once a week on the fleshing machine during the reliming period, is helpful. Increasing the quantity of the bate or the amt. of acid used in pickle is not helpful. A complete procedure is given. Yields and analytical and physical test data are tabulated. The leather should have a minimum tensile strength of 100 kg. per sq. cm., stitch tear 50 kg. per cm., extension at break 60%, and extension of 30% under a 2.5 kg. load. H.B.M.

Polyamide as Chromatographic Adsorption Material. G. Reich and W. Bartel. *Ges. Abhandl. deut. Lederinst. Freiberg/Sa.*, **No. 14,** 27–33 (1959).—Polyamides adsorb through formation of H-bonds and thus are analogous to collagen in many respects. The sorption curves of phenol on hide powder and polyamides are similar in shape, although polyamide has a higher sorption capacity. Tests with dyes show that sorption by polyamide decreases with increased no. of SO_3H groups in the dye, and increases with no. of substantive groups. Polyamides can be used to separate sulfonation products of phenols and to separate methylol compounds from dihydroxydiphenyl sulfone. A great advantage of polyamide is that water can often be used as eluant; if not, dilute methanol may be used. H.B.M.

Statistical Planning and Evaluation of Research in the Realm of Leather. G. Reich and R. Steinhardt. *Ges. Abhandl. deut. Lederinst. Freiberg/Sa.*, **No. 14,** 35–44 (1959).—An elementary exposition. H.B.M.

Simple Apparatus for Ascertaining the Area Stretch of Leather. G. Reich and A. Meissner. *Ges. Abhandl. deut. Lederinst Freiberg/Sa.*, **No. 14,** 45–54 (1959).—The method is that described by Merrill (*JALCA*, **34,** 5 [1939]) using the Stather-Herfeld water permeability apparatus equipped with a rubber diaphragm instead of a Mullen tester. Illustrative pressure-stretch curves are given. H.B.M.

Chemical and Electron-Optical Investigations on the Reaction of Basic Chromium-III-Complexes with Collagen. K. Kühn and E. Gebhardt. *Leder*, **11,** 148–52 (1960).—Collagen fibers from Achilles tendons were given various treatments—guanidation, deaminization, deaminization and acetylation,

methylation, methylation and deaminization, or methylation, deaminization and acetylation—to modify the side chains. They were then tanned with basic chrome alum (cationic), $CrCl_3$ plus 6 equivalents of Na_2SO_3 per Cr (anionic), or Na tetraoxalate diol chromate (anionic). The tanned fibers were examined in the electron microscope for cross striation, and shrinkage temperatures and Cr contents were determined. The Na tetraoxalate diol chromate had no tanning action at all unless it was partially hydrolyzed by treatment with acid, because the complex is too stable. All the fibers in which the COOH groups were intact (not methylated) showed marked cross striations after tanning, no matter whether the tanning agent was cationic or anionic, and none of the methylated fibers showed anything but blurred striations. Modification of basic or hydroxyl groups had little or no effect. This was true also of Cr fixation and elevation of shrinkage temperature, though shrinkage temperatures could not be measured for methylated fibers because they were excessively swollen. Decarboxylated fibers fixed very little Cr from basic Cr alum (as expected), or from acidified tetraoxalatochromiate, but they did fix appreciable amounts from the sulfitochromiate. However, in this last case the decarboxylated fibers fixed only about a fifth as much Cr as did acid-swollen native collagen. It is concluded that the highly subdivided cross striations are produced by cross-linking of COOH groups through Cr, whether the Cr complex was originally cationic or anionic. H.B.M.

Recent Investigations on Aldehyde Tannage in the U.S.A. E. M. Filachione. *Leder*, **11**, 141–43 (1960).—A summary of work done at the Eastern Regional Research Laboratory and at the QM Research and Development Laboratory, most of which has been published in *JALCA*. H.B.M.

The Production of Loose Grain in Shoe Upper Leather through the Combined Action of Stretching (Lasting), Gluing to the Lining Leather, and the Adhesive. W. Ackermann. *Leder*, **11**, 152–53 (1960).—It has been known that otherwise tight-breaking leathers sometimes break loose, or even pipey, after being pasted to the lining. This effect is not always apparent until the leather is stretched. A simple test to determine whether a given adhesive will induce loose break is described. Leather strips, about 15 x 3 cm., are pasted to the lining (or just the adhesive is applied), dried, and stretched 20% for 5 min., resulting in about 10% permanent increase in length. Then the leather is tested as usual for looseness. H.B.M.

Chemical Investigations on the Carbohydrate Groups of Collagen. H. Hörmann. *Leder*, **11**, 173–79 (1960).—While the amino sugars, which obviously come from the mucopolysaccharides of the interfibrillary substance, are rapidly and completely removed by treatment with dilute alkali, a large part of the hexoses is retained very tenaciously. Citrate-soluble collagen can be freed completely from amino sugars by repeated precipitation or by shaking out with $CHCl_3$, while most of the hexoses are retained after these treatments. Contrary to the belief of Mikhailov *et al.*, the fibrils obtained from soluble collagen free from amino sugars do show crossbanding, though the contrast is very slight and is much improved by adding mucopolysaccharide. When collagen is partially denatured by heat and digested with trypsin, all of the hexoses remain in the small insoluble residue. After repeating these treatments

the residue amounted to only 1.56% of the original collagen and contained 32% hexoses and only 2% nitrogen. It is suggested that the hexose molecules form cross links between polypeptide chains, being bound to one chain by a glucoside bond, probably through O, and to either one or two different chains by ester linkage with carboxyl groups. Most of the hexose is removed from soluble collagen by oxidation with HIO_4 in 0.1% acetic acid. The polypeptide chains are not broken; only side chain amino acids are attacked. Collagen is dissolved at room temperature by *simultaneous* action of HIO_4, 10% acetic acid, and 8*M* urea; successive treatments with these reagents in any order is ineffective. Probably these reagents act on the glucoside linkage. Similarly, collagen is dissolved by simultaneous action of hydroxylamine and KCNS or LiBr, which act on ester linkages. H.B.M.

Methods for Determining Gums in Wattle Bark Extract. E. A. Maihs and D. G. Roux. *Leder*, **11**, 179–83 (1960).—Wattle extract contains 6 to 7% of vegetable carbohydrate gums, which contribute to the high viscosity and tendency to sludge formation in the tan liquors. Part of the gum is adsorbed by hide powder along with tannin. Two methods of determining gum are described. In the first, about 10 g. of powdered extract is extracted in a Soxhlet apparatus (Soxhlet tube cooled) for 2 hr. with an azeotropic mixture of dioxane and water, or for 16 hr. with anhydrous acetone. These extractions yielded 7.8 and 6.4%, respectively, of residue that tested free from tannin with $FeCl_3$. Longer extraction with dioxane resulted in partial solution of the gum. Of other solvents tried, anhydrous methanol dissolved the gum, and azeotropic mixtures containing ethanol, isopropanol, *tert.*-butanol, or methylethyl ketone did not yield tannin-free residues. In the second method, 10 ml. of a 10% solution of extract is treated in a centrifuge tube with 200 ml. acetone or azeotropic dioxane, shaken, centrifuged, decanted, and the residue washed twice with the solvent, and finally dried and weighed. The percentages of residue found by this precipitation method were practically the same as by the extraction method. The residue contains 10–12% ash which must be subtracted from the weight of the residue. Determinations of methoxyl groups and nitrogen indicate that the residue contains small amounts of lignin and protein. Gums may be determined in the residue by hydrolyzing and determining reducing sugars by the usual methods. H.B.M.

The Manufacture of Sole Leather with the Use of Higher Proportions of Synthetic Tanning Materials. F. Stather, G. Reich, and J. Überla. *Ges. Abhandl. deut. Lederinst. Freiberg/Sa.*, **No. 15**, 5–15 (1959).—Eastern Germany produces only 30% of its vegetable tannin requirement, and this consists solely of pine bark tannin. Synthetic tanning materials now constitute 45–50% of the total tannin consumed. A description is given of large-scale experiments that were undertaken to see if imports of vegetable tannins could be still further reduced by using 70–100% syntans. These experiments were carried out in tanneries and extended over 2 to 2½ years. The syntans employed were (1) Pellutan EZE, a mixed condensate of dihydroxydiphenyl sulfone, phenolsulfonic acid, ligninsulfonic acid, and HCHO, (2) Pellutan G40, a condensation product of polyhydroxyphenols, ligninsulfonic acid, and HCHO, and (3) Wofagan M, an ω-sulfonated cresol-HCHO resin with beechwood sulfite liquor. In 4 tests, these syntans were used in about equal amounts; in the 5th, Pellutan EZE and G40 were used in the ratio 4:1. From 48 to 100%

total syntan was used, with 20–30% pine bark extract, and 0–24% of a blend of oakwood, quebracho, chestnut, wattle, and valonea, of which oakwood constituted half—all calculated on the total tannin basis. Tannage was done by the procedures used in the tanneries in question and included a series of suspenders, layaway vats, and finally drum tannage. Total time was from 85 to 153 days. Data are presented for liquors and leather. In all the tests, the leather yield and degree of tannage declined with time, while time of tannage and, to some degree, consumption of tannin increased. Use of more than 50% of syntans in the blend will necessitate drastic changes in tanning methods.

H.B.M.

The Different Behavior of Syntans and Vegetable Tannins During Continuous Feeding in Pit Tannage. F. Stather, G. Reich, J. Überla, and W. Barthel. *Ges. Abhandl. deut. Lederinst. Freiberg/Sa.*, **No. 15,** 16–33 (1959).—Pieces of dehaired, delimed cattlehide were tanned in the laboratory in 7 different series of liquors—4 containing a single syntan (Pellutan EZE, Pellutan G40, Wofagan M [see preceding abstract] and Wofagan E [condensation product of 2-naphtholsulfonic acid, a phenolic oil, and HCHO]); 1, pine bark extract; 1, a blend of oakwood, quebracho, chestnut, and wattle extract (3:1:1:1); and 1 containing 50% of syntans (equal parts of Pellutan EZE, G40, and Wofagan M) 30% pine bark extract, and 20% of the above vegetable tan mixture. Each laboratory tan lot passed through 8 suspenders (3 days in each) and 3 layaway liquors (18 to 24 days in the 1st and 27 days in the 2nd and 3rd)—total tanning time 96–102 days. Initially, all 7 sets were made up to the same tannin concentrations, increasing gradually from tail suspender to head layaway; thereafter, the tail liquor was discarded after each lot, and all tannin was added in a fresh head suspender. Each lot was given 33% tannin on the white weight. The whole experiment took 8 months. Liquors and leathers were analyzed at various stages of tanning. After equilibrium was established, it was evident that the tail liquors of the syntan series were much higher in tannin (by hide powder analysis) than the corresponding liquors of the vegetable tannin series. But analyses by the amine precipitation method (see abstract, *JALCA*, **54,** 534 [1959]) showed that the tail syntan liquors actually contained little or no true tannin. Analyses of the syntan leathers showed that most of the true tannin was taken up in the head layaway, and that the long tannage in dilute liquors merely accomplished a certain amount of filling. The syntan leathers had lower degrees of tannage, but the leather tanned with 30% syntan had the highest. Physical tests showed no pronounced differences except that the syntan leathers had low sweat resistance. When calfskin pieces were tanned in liquors of varying concentration, incipient leathering took place in vegetable liquors containing only 8 to 20 g. tannin per liter, while 40 to 70 g. tannin per liter was required to give the same effect with syntan liquors. In tanning with syntan, it will be necessary to increase the total amount of tannin given (figured from hide powder analysis) and to discard tail liquors at much higher apparent tannin concentration than in the case of vegetable tannins. By so doing, the tanning time can be shortened materially.

H.B.M.

The Use of Aromatic Syntans in Tanning at Elevated Temperature. F. Stather, G. Reich, and G. Zimmermann. *Ges. Abhandl. deut. Lederinst. Freiberg/Sa.*, **No. 15,** 34–39 (1959).—Leather tanned at about 40°C. with mixtures

containing syntans is notoriously weak. Seven commercial syntans, 2-naphtholsulfonic acid and its condensation product, ligninsulfonic acid, and 4 vegetable tannins were tested by Vago's method (see abstract, *JALCA*, **54**, 233 [1959]) by digesting thin, dehaired skin specimens in 17° Baume solutions for 6 weeks at 40°C. None of the vegetable tannins produced any damage. Five of the syntans, ligninsulfonic acid, and especially 2-naphtholsulfonic acid and its condensation product caused more or less damage, but 2 syntans did not. These were Wofagan M and Pellutan G40, which are notably low in sulfonic acid groups. Leather pieces were tanned with 3 vegetable tannins and 3 syntans, at 20°, 30° and 40°C., either without pretannage or following pretannage with either Cr or HCHO. The tensile strengths of the vegetable leathers and the Pellutan G40 leather were practically unaffected by temperature of tannage and little affected by pretannage, but the tensile strengths of the other 2 syntan leathers tanned at 40°C. without pretannage were very low. Pretannage with Cr prevented this damage in both cases, and pretannage with HCHO did so in one case but not the other. As a general precaution, syntans should be used at temperatures not exceeding 35°C., preferably with prechroming.

H.B.M.

Accelerated Sole Leather Tannage through Pretannage with Metal-Tannin Complexes. F. Stather, G. Reich, and S. Walther. *Ges. Abhandl. deut. Lederinst. Freiberg/Sa.*, **No. 15**, 40–49 (1959).—Pretannage with a mixture of syntan and chrome liquor, before tanning with strong vegetable or syntan liquors, is claimed to give more uniform vertical distribution of Cr than pretannage with Cr alone. Tests showed that 9 out of 13 syntans tested were compatible with Cr alum (freedom from precipitation), and 2 more were compatible when masked with Na_2SO_4. Five out of the 13 were compatible with K alum. Tanning tests were performed, using 32 different pretannages with mixtures of Cr alum or K alum with various syntans, followed by tannage in a set of 7 liquors for 28 days using a mixture of 50% syntan (blend of 3) and 50% vegetable tannin (mostly pine bark). The Cr or Al content of grain, middle, and flesh splits and shrinkage temperature were determined after pretannage, and degree of penetration, yield on white weight, strength, and stretch were measured after tanning. Penetration and yield could not be related to total metal uptake or uniformity of metal distribution, both of which varied widely, but in a general way the mixtures of Cr alum with auxiliary syntans gave better results than mixtures with replacement syntans. Tanning tests were carried out with a mixture of vegetable tannins, a mixture of vegetable and synthetic tannins, and 2 different syntans, following pretannages with Cr alum, alone or blended with 6 different syntans or similar products, or with a commercial Cr-syntan concoction. Penetration was measured daily. After 7 days, penetration was complete for the straight vegetable liquor in all cases (including no pretannage at all!), and was incomplete for the vegetable-syntan mixture and for Pellutan AE in all cases. For these tannages, pretannage with either Cr alum + condensed naphthalene sulfonic acid or Cr alum + Pellutan G40 + 2 Na_2SO_4 improved penetration slightly. For tannage with Pellutan G40, penetration was complete or nearly so in all cases. Degree of tannage was determined for some of these leathers. Pretannage with Cr alum alone, Cr alum with condensed naphthalene sulfonic acid, or the commercial pretanning agent gave increased tannin fixation from the vegetable tannin blend, and from both syntans, and Cr alum alone was most effective in all 3

cases. Fixation from the syntan-vegetable tannin blend was decreased, if anything, by pretannage. Tan values were measured for hide powder, after various pretannages and after subsequent tannage with Pellutan G40. The final tan value, compared to non-pretanned hide powder, was increased considerably by pretannage with Cr alum alone or with Cr alum + Pellutan G40 + 2 Na_2SO_3 and was not materially affected by the commercial pretan compound or by Cr alum + condensed naphthalene sulfonic acid. Porosity of the leathers after pretannage, determined by measuring the permeability to water under 0.5 atmosphere pressure, is not a reliable index of the effectiveness of pretannage, as claimed by Michailov, but permeability to 6*N* NaCl solution, which prevents acid swelling, is such an index. H.B.M.

A Simple Method for Measuring the Complexing Affinities of Aromatic Tanning Materials and Dyes toward Chromium (III) Salts. G. Reich, S. Walther, and F. Stather. *Ges. Abhandl. deut. Lederinst. Freiberg/Sa.*, **No. 15,** 50–53 (1959).—The method of Otto (abstract, *JALCA*, **54,** 477 [1959]) in which the materials under study are adsorbed on a column of precipitated $Cr(OH)_3$ has been modified. Increasing quantities of the dye or tanning material are mixed with identical quantities of $Cr(NO_3)_3$ solution, after which NaOH is added to precipitate $Cr(OH)_3$, the solutions are boiled and filtered and the filtrate is examined for dye or tanning agent. The amount of the substance under study that can be complexed by the fixed amount of Cr is the largest quantity of that substance that is coprecipitated completely. Dye filtrates are examined visually, and tanning agent filtrates by testing with Cd acetate and pyridine. The effects of structure on the complex-forming capacity of dyes and the effects of such masking agents as phthalate and resorcinolate in inhibiting complex formation were studied by this method. The results were in agreement with those reported by Otto (abstract *JALCA*, **54,** 422 [1959]). H.B.M.

Manufacture of Suede Garment Leather from E.I. (Vegetable-tanned) Sheepskins. T. S. Krishnan and P. S. Venkatachalam. *Bull. Central Leather Research Inst. Madras*, **6,** 434–37 (1960).—The leather is stripped with borax, bleached with oxalic acid, Calgon, and a bleaching syntan, and retanned with Cr to a shrink temperature of 100°C. After the skins are neutralized and fatliquored, they are dried, crusted and buffed, wet back with Na lauryl sulfonate, dyed, and treated with a chrome waterproofing compound. H.B.M.

Report of the Research Institute for the Leather Industry in Vienna for the years 1955–59. J. A. Sagoschen. *Leder Kurier*, **4,** 132–37, 139–45 (1960).—This report of the activities of the institute includes tabular data on a vast number of tannin analyses. H.B.M.

PATENTS

Waterproofing and Coating Leather and Other Surfaces. Brit. Pat. 831,020. Midland Silicones Ltd. Appl. Oct. 2. 1957.—Leather, tanned, tawed or otherwise cured, and either finished or unfinished, and of any type such as horsehide, pigskin, kid and cowhide, is rendered water-repellent by treatment with a composition comprising (1) 50 to 85% (by weight) of a siloxane composed of units of the general formula $R_n^{III}SiO_{\frac{4-n}{2}}$ wherein each R^{III} is a monovalent hydrocarbon or halogenated hydrocarbon radical n is 0, 1, 2 or 3 and the average ratio of R^{III}/Si in the siloxane is from 0.9 to 3.0; and (2) 15 to 50% of a β-dicarbonyl zirconium compound containing an average of 0.75 to 4.0 β-dicarbonyl groups per Zr atom (*see* Groups IV (a) and IV (b)). The compositions are preferably applied in solution, e.g. in toluene, xylene, methylene chloride or perchlorethylene, by dipping, brushing or spraying. A preferred composition consists of a mixture, by weight, of (1) 15 to 50% of a β-dicarbonyl Zr compound; (2) 5–70% of a methylpolysiloxane composed of $(CH_3)_2SiO_{\frac{2}{2}}$ and $SiO_{\frac{4}{2}}$ units; and (3) 5 to 80% of a siloxane of the formula $Z_mSiO_{\frac{4-m}{2}}$ wherein each Z is a hydrocarbon radical of less than 7 C atoms and m has an average value of from 2 to 2.9. Examples are given of leather impregnated with the compositions. Glass, ceramic and other surfaces may also be rendered water-repellent. In Example 2, unfinished leather which had been rendered water-repellent by impregnation with the above composition, was coated with a composition composed of 60% (by weight) of water, 20% of propylene glycol, 10% methyl methacrylate and 10% black pigment, and after drying was further coated with a composition consisting of 55.6% of water, 11.1% of casein-shellac solution, 5.5% of carnauba wax, 13.9% of a methylmethacrylate resin and 13.9% of pigment. After drying a top coating comprising 50% of nitrocellulose lacquer and 50% of water was applied. Specifications 773,347 and 804,162 are referred to.

Mothproofing of Keratinaceous Materials. U. S. Pat. 2,945,735. L. M. Kozloff, Chicago Ill., assignor, by direct and mesne assignments, of seventy percent to Hightower-Morse & Company, Chicago, Ill., a corporation of Delaware, ten percent to B. Wolnak, Highland Park, and five percent to J. P. Antonow, Chicago, Ill. Filed Dec. 17, 1957.—12. A process of mothproofing and dyeing wool which comprises contacting wool with an aqueous solution containing acid wool dyes and pyridine-3-sulfonic acid under acid conditions to produce a dyed wool having pyridine-3-sulfonic acid impregnated therein.

Mothproofing of Keratinaceous Materials. U. S. Pat. 2,945,736. L. M. Kozloff, Chicago, Ill., assignor, by direct and mesne assignments, of seventy percent to Hightower-Morse & Company, Chicago, Ill., a corporation of Delaware, ten percent to B. Wolnak, Highland Park, and five percent to J. P. Antonow, Chicago, Ill. Filed Dec. 17, 1957.—4. A method of controlling the larvae of *Tineola bisselliella* which comprises contacting the wool habitat of

said larvae with an aqueous solution containing acid wool dyes and benzimidazole wherein said solution is maintained at a pH of less than about 2, to produce a dyed wool containing at least about 0.5% benzimidazole by weight thereof.

Method of Dehairing Hides. U. S. Pat. 2,945,737. T. C. Thorstensen, Chelmsford, Mass., assignor to Tanners' Council of America, Inc., New York, N. Y., a corporation of New York. Filed Apr. 25, 1957.—1. The process of dehairing cattle, sheep and goat hides in such fashion as to produce recoverable hair without damage to the hides, which comprises treating wet hides with a first, lime-free, bath comprising an aqueous alkaline solution of 2 to 10%, based on hide weight, of an alkali metal salt which has a reducing action strong enough to reduce the S—S linkage in cystine, for a period of at least an hour, the pH of the bath being maintained at a point not above 11.0 for substantially but not necessarily the entire treatment period, removing the first bath, treating the hides for a few hours at ordinary ambient temperatures with a second bath comprising a lime-free aqueous alkaline solution containing ammonium ions representing at least 0.15% NH_3 and sodium ions, and maintained during the treatment at a pH of at least 10 and under 12.0, and then mechanically separating the loosened recoverable hair from the hides.

Oil Base Fat-Liquor Composition with Polybasic Acid Ester and Method of Use. U. S. Pat. 2,950,950. J. Plapper, R. Heyden, and G. Arnold, Dusseldorf, Germany, assignors to Bohme Fettchemie G.m.b.H., Dusseldorf, Germany, a corporation of Germany. Filed June 24, 1954.—7. A fat-liquoring composition for chrome-tanned hides and skins, comprising an oil base and about 2 to 20% of a masking agent selected from the group consisting of acidic higher aliphatic alcohol mono-esters of poly-basic acids, selected from the group consisting of tri- and tetra-basic acids wherein the alcohol radical contains from 12 to 18 carbon atoms, and salts thereof, said masking agent containing at least two free acid groups and being soluble in said oil base.

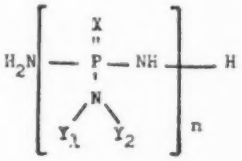
New Dyeing Process. U. S. Pat. 2,950,165. H. R. Hadfield, B. Batterbee, and D. Lemin, Manchester, England, assignors to Imperial Chemical Industries Limited, Millbank, London, England, a corporation of Great Britain. Filed Sept. 10, 1957.—1. Process for coloring textile materials selected from the class consisting of protein and regenerated protein textile materials with a water-soluble di-chloro-s-triazinyl amino dyestuff containing as the chromophoric group a member selected from the class consisting of azo and anthraquinone chromophoric groups, which comprises applying the said dyestuff to the said textile material in an aqueous medium at a temperature from about 0°C. to about 55°C., in conjunction with a treatment with an acid-binding agent selected from the group consisting of water-soluble carbonates and bicarbonates in a dilute aqueous solution.

Process for Dressing Leather. U. S. Pat. 2,950,216. G. Kolb, Koln-Stammheim, and K. Eitel, Leverkusen, Germany, assignors to Farbenfabriken Bayer Aktiengesellschaft, Leverkusen, Germany, a corporation of Germany. Filed June 1, 1955.—1. A process of dressing leather which comprises treating

the leather with an aqueous emulsion of a copolymer of at least 45% by weight of a conjugated butadiene and at least 10% by weight of 1,1-dichloroethene.

Treatment of Tanned Hides and Leather with Polymers of Vinyl and Diene Monomers, Emulsifiers and Tanning Agents. U. S. Pat. 2,949,335. G. Mauthe, Opladen, W. Graulich Leverkusen-Bayerwerk, and H. Röhling, Leverkusen, Germany, assignors to Farbenfabriken Bayer Aktiengesellschaft, Leverkusen, Germany, a corporation of Germany. Filed Mar. 7, 1956.—1. The process which comprises contacting tanned hides and leather with an aqueous emulsion of a member selected from the group consisting of homopolymers and copolymers of vinyl- and diene-monomers and with at least 2% of a member selected from the group consisting of anionic, non-ionic, and cationic emulsifiers in the presence of at least one tanning agent selected from the group consisting of anionic vegetable and synthetic tanning agents, said synthetic tanning agents being phenolic-hydroxyl-group-containing and sulfonic-acid-group-containing tanning agents, said contacting being conducted in a medium selected from the group consisting of a neutral, an acid, and a weakly alkaline medium, so as to preserve the acidity of the leather.

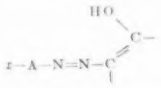
Fireproofing Textiles &c. Brit. Pat. 830,800. Farbenfabriken Bayer A.G. Appl. April 4, 1957.—Compositions for fire-proofing permeable materials comprise amido-phosphoric acid derivatives of the general formula



wherein X represents oxygen or sulphur, Y_1 and Y_2 each represent a hydrocarbon radical which may be saturated or unsaturated, aliphatic, cycloaliphatic, aryl or aralkyl and may be substituted e.g. by halogen, or Y_1 may be hydrogen or Y_1 and Y_2 together with the nitrogen atom form a heterocyclic radical, e.g. an ethyleneimine, pyrrolidine, piperidine, hexamethyleneimine or morpholine radical, and n denotes any integer. They may be used in solution in solvents such as water, alcohols, esters, ketones, hydrocarbons or halogenated hydrocarbons or as dispersions. Heat treatment at 100–150°C. may be effected after impregnation. Textiles, wood, cardboard, leather and plastics may be treated. Other substances which may be present include isocyanates and condensation products of formaldehyde, e.g. with urea, guanidine, dicyandiamide or melamine.

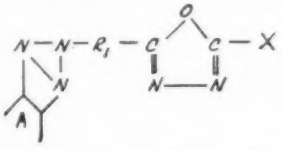
Monoazo Dyestuffs and Their Metal Complex Compounds. U. S. Pat. 2,928,823. O. Senn, Arlesheim, near Basel, H. Uehlinger, Binningen, and W. Wehrli, Riehen, near Basel, Switzerland, assignors to Sandoz Ltd., Basel, Switzerland, a Swiss firm. Appl. Aug. 13, 1958.—1. A member selected from the group consisting of a monoazo dyestuff which is free from sulfonic acid

groups, is free from carboxylic acid groups standing in a position other than ortho to the azo group and corresponds to the formula



and the chromium and cobalt complex compounds thereof, wherein *x* stands in ortho-position to —N=N— and represents a member selected from the group consisting of a hydroxy and a carboxy group,

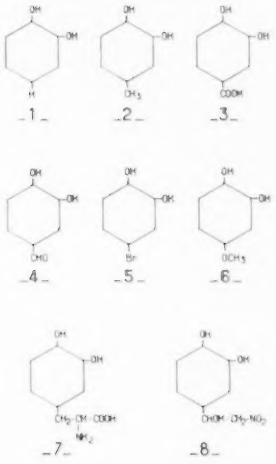
represents the radical of a member selected from the group consisting of 1-hydroxy-acenaphthene, 9-hydroxyphenanthrene, 2-hydroxyindole, 2-hydroxy-5,7-dibromoindole, 1-methyl-2-hydroxyindole and 1-acetyl-2-hydroxyindole, and



A represents a member selected from the group consisting of a further unsubstituted benzene radical and a further substituted benzene radical, the substituents being selected from the group consisting of methyl, chlorine, nitro, methylsulfonyl, sulfonic acid amide, sulfonic acid lower alkylamide, sulfonic acid lower hydroxyalkylamide, sulfonic acid lower alkoxyalkylamide, sulfonic acid phenylamide, sulfonic acid cyclohexylamide and sulfonic acid morpholide. Useful for coloring wool and leather.

Tanning Agent. U. S. Pat. 2,946,649. R. Heyden, Dusseldorf, Germany, and F. Schmitt, deceased, late of Dusseldorf, Germany, by A. Schmitt, née Neukirchner, Dusseldorf, Germany, heir, assignors to Boehme Fettchemie G.m.b.H., Dusseldorf, Germany. Filed July 20, 1956.—1. A process for tanning skins, hides and furs into leather, which comprises milling into these materials from 1 to 8 percent of the polyalkyl ether condensation product obtained by the condensation of from 6 to 18 mols ethylene oxide with one mol of an alkylated sulfamide selected from the group consisting of alkylated benzene sulfamides and alkylated naphthalene sulfamides, the alkyl radical being selected from the group consisting of butyl, hexyl, octyl, dodecyl and octadecyl radicals, adjusting the pH range during milling to 2 to 9, until tanning occurs, and washing the excess tanning agent from the leather after tanning is complete.

Process for Dyeing Keratinous Material with Ortho-Diphenols. U. S. Pat. 2,944,869. G. Kalopissis and G. Ghilardi, Paris, France, assignors to Societe Anonyme dite: Societe Monsavon-L'Oreal, Paris, France, a corporation of France. Filed Jan. 17, 1958.—



1. A process for dyeing hair and other keratinous materials which comprises applying thereto an aqueous solution consisting of at least one orthodiphenol of the general formula:

wherein R is selected from the class consisting of the hydrogen atom, the halogen atom, aldehyde, alkyl, carboxy, alkoxy, nitro-hydroxyalkyl and alpha amino propanoic groups, and an oxidizing agent selected from the class consisting of ammonium and alkali metal iodates, periodates and persulphates.

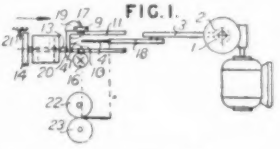
Method of Hardening Shellac and Gum Arabic. U. S. Pat. 2,929,732. I. Kowarsky, University City, Mo., assignor to Universal Match Corporation, St. Louis, Mo., a corporation of Delaware. Original appl. April 10, 1950, Patent No. 2,722,484. Divided and this application October 31, 1955.—3. The method of forming a hardened gum arabic from an aqueous solution of solubilized gum arabic which comprises forming an aqueous solution containing the solubilized gum arabic, a sulfite, a volatile alkali, and an oxidizing agent selected from the class of inorganic salts of chromium wherein the chromium is in the hexavalent state and is capable of being reduced to the trivalent state, adjusting the alkalinity of such solution to a pH in excess of 8.5, and evaporating the volatile alkali from such solution when it is desired to produce a hardened gum arabic. Also useful for hardening proteins.

Impregnating Leather with Polyurethanes. Brit. Pat. 830,841. Farbenfabriken Bayer A.G. Appl. Sept. 27, 1957.—A solution in an organic solvent

containing both a di-isocyanate-modified polyhydroxy compound having free hydroxyl groups, and also a polyisocyanate, is applied to leather during or after its dyeing or colouring with a soluble or insoluble dye or insoluble pigment. Leather treated in this way exhibits an improved "handle," resistance to rubbing, and water-repelling properties, and the dyeing is fast to washing and dry-cleaning. Preferably the solution also contains an accelerator for the reaction between the modified polyhydroxy compound and the polyisocyanate, and the dye or other colouring matter may be dissolved or dispersed in this solution. Insoluble inorganic or organic pigments, or dyestuffs soluble in the solvents used for the solution, as for example cellulose acetate disperse dyes, or chromium-containing metallized dyes, may be used. The di-isocyanate modified polyhydroxy compound is prepared by reacting polyhydroxy compounds of relatively high molecular weight, e.g. polyesters of dicarboxylic acids and dihydric and polyhydric alcohols, with di-isocyanates, e.g. toluylene-, hexamethylene-, *p*-phenylene, or 4,4-diphenyl-methane-di-isocyanates. The di-isocyanate is used in a proportion such that the di-isocyanate-modified polyhydroxy compound obtained still has free hydroxyl groups so that, when applied to the leather, it cross-links with the polyisocyanate added to form a product impervious to water and organic solvents used in dry-cleaning. Suitable polyisocyanates include known monomeric polyisocyanates, and reaction products of polyhydric alcohols and di-isocyanates which still contain isocyanate groups as, e.g., those of 1 mol. of hexanetriol with 3 mols. of toluylene- or hexamethylene-di-isocyanate. Suitable solvents include ethyl acetate, acetone, the methyl ether of glycol acetate, trichlorethylene, methylene chloride, benzene, and mixtures of these. The solution may be applied by spraying or dipping, and drying and cross-linking may be accelerated by gently heating the leather. Accelerators which may be added to the solution include organo-metallic compounds, e.g. of the titanic acid-stearyl alcohol ester type, in conjunction with reaction products of phenyl isocyanate with tertiary amines.

Splitting-Machines. Brit. Pat. 830,892. Albeko Schuhmaschinen-G.m.b.H. Appl. Oct. 23, 1958.—

FIG. 1.



In a leather splitting machine comprising rollers 19, 20 for feeding the leather to an endless band knife 4 the cutting edge 4' of which is constantly sharpened by means of grinding wheels 22, 23, adjusting mechanism for the knife to compensate for wear due to abrasion comprises a U-shaped member 11 having a pair of vertically spaced marks 9, 10 disposed on the limbs thereof, the member 11 being adjustable horizontally relative to the vertical plane passing through the axes of the feed rollers, and means for horizontally adjusting the band knife so that its cutting edge will touch the vertical plane passing through the marks 9, 10. The member 11 is adjustable by means of a screw spindle 13 which carries a graduated dial 14 co-operable with a fixed pointer 21. The band knife is carried by guides 18 adjustable by means of pivotally-mounted bell-crank levers 3 having rack teeth engageable by worms 2 on a motor-driven shaft 1. The marks 9, 10 are preferably in the form of slits having associated

therewith a light source 16 and a selenium cell 17, the arrangement being such that when light passes through both slits and impinges on the selenium cell, the shaft 1 is automatically rotated until the cutting edge of the band knife touches the vertical plane passing through the slits whereupon rotation of the shaft 1 is automatically stopped. The grinding wheels are adjustable towards and away from each other and may be mounted so as to be adjustable together with the band knife guides.

BOOK REVIEW

Gerbereimaschinen. A. C. Brill. Darmstadt. Eduard Roether Verlag 1960. 228 pp.; cloth. 24.-DM.—The publication in Germany of a highly practical book on tannery machines should be of interest to anyone connected with leather manufacture in the United States. Tannery equipment is offered by about one third of the advertisers in "Das Leder", the leading scientific journal for leather technology in Continental Europe. By contrast, the same kind of journal in this country and a monthly trade magazine widely read by tannery engineers and chemists regularly carry no more than 2 or 3 advertisements offering tannery equipment. This difference in emphasis explains the fact that the publisher of "Das Leder" has followed H. Loewe's introductory book on leather chemistry (see *JALCA*, **55**, 63, [1960]) with a book of similar scope on tannery equipment, both books addressing themselves primarily to high-school or college graduates who want to educate themselves in their newly-chosen field.

A. C. Brill, the author of the new book, is known to readers of "Das Leder" as an expert who is equally well qualified to write about the Russian worm gear drum and the American Secotan process. After speculating about these attempts at automation, he has now turned to more conventional tannery equipment, and thanks to his background as a specialist who has built and installed tannery machinery for half a century and as a consulting engineer of renown and competence, he is also fully suited for this difficult task.

In dealing with the subject matter, Brill has divided his book into four sections of unequal length. He begins with a 10-page discussion of electric motors and drives. Next he takes 19 pages to describe the functional elements of machines, e.g., gears and chains, couplings, brakes, bearings, greasing devices, machine greases, and finally the various types of knives and grinding machines.

These two sections prepare the reader well for the next 156 pages devoted to tannery machines proper. These are presented on the basis of common structural elements rather than in the order a visitor would meet them in a tannery, following the making of leather from the beamhouse to the sorting room. Thus the author reviews first the machines into which hides or skins are fed on revolving cylinders. Next he discusses machines that provide a flat surface on which hides are spread in preparation for a particular process.

Here we find the splitting machines which deserve special mention since their description reflects on every page the personal experience of the author. Furthermore the different types of coating machines and drying tunnels are discussed, followed by a consideration of presses and measuring machines. An excellent chapter on paddle wheels and tanning drums concludes the machine section. In the final 10 pages of text the reader is introduced to the author's ideas on the construction of a side leather factory including floor plan, production schedules, and arrangements for future expansion. Here we become aware of a striking difference between the European and American economy. In the U.S. the building of a new plant designed for soaking 300 hides per day could hardly be called economically sound; however, in many countries this size would be adequate to assure profitable operations.

A subject index of four pages increases the usefulness of the book, but author and patent indices are lacking, although names of machine factories and of inventors are scattered throughout the text. Outstanding contributions on the part of the United States to the international advances in the mechanization of tannery operations are duly acknowledged.

The truly outstanding feature of Brill's book is its excellent illustrations, which are almost equal in number to the pages. At least half of the illustrations are fine drawings or sketches that support the explanation of the various machines. The photographs are rich in contrast, without any distractive background, in many instances showing only the working parts in order to facilitate comprehension.

The illustrations in this book are especially important in that they enable an engineer with only a general reading knowledge of German to acquire the technical vocabulary needed to penetrate into the related text. In this age of specialization, it would certainly be a credit to the chemist, who often takes some German courses in college, to cooperate with the engineer in this respect, and in doing so he would surely find his own reward. In other words, a book as original and as instructive as Brill's should be added to the library of any tannery which has means of bridging the language barrier.

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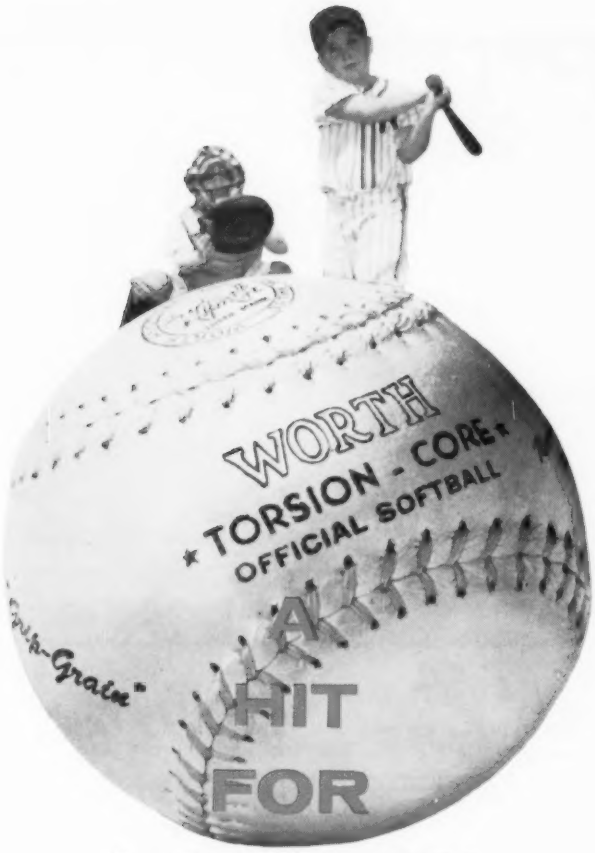

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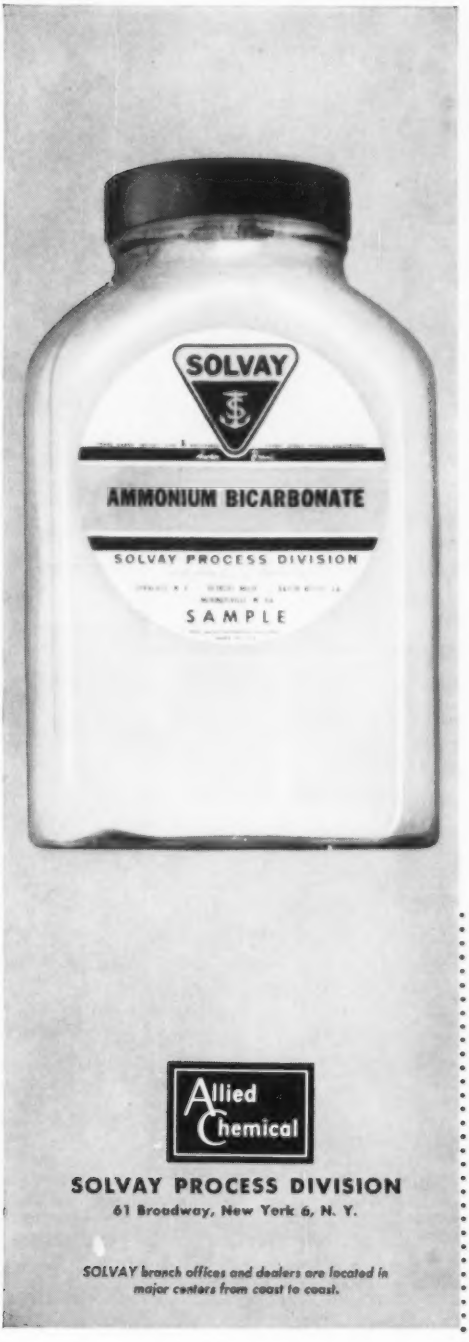

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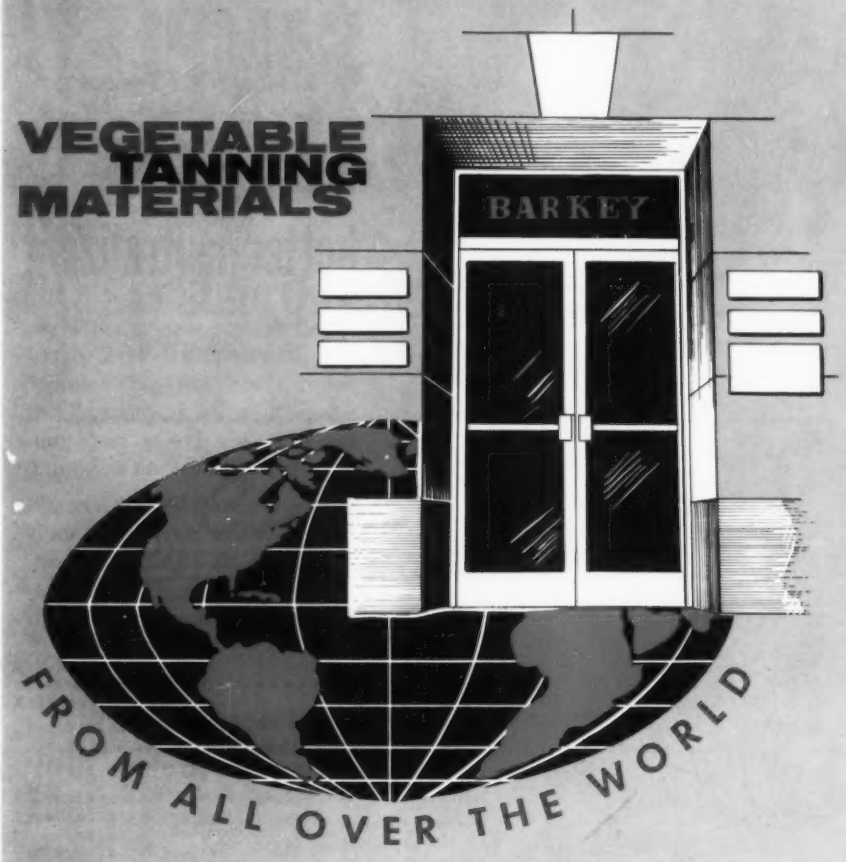

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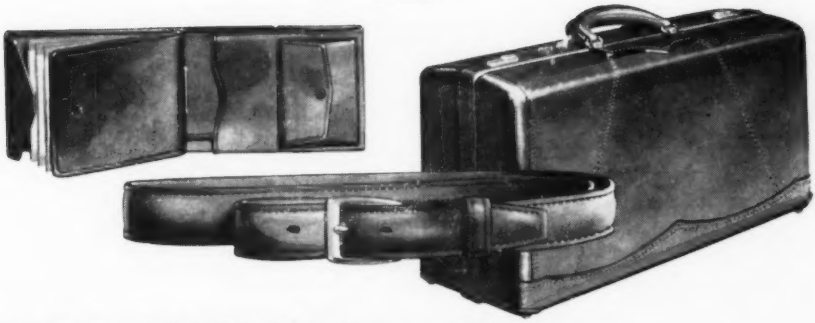

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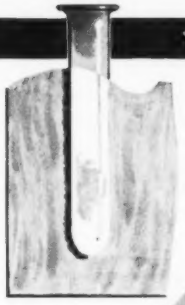

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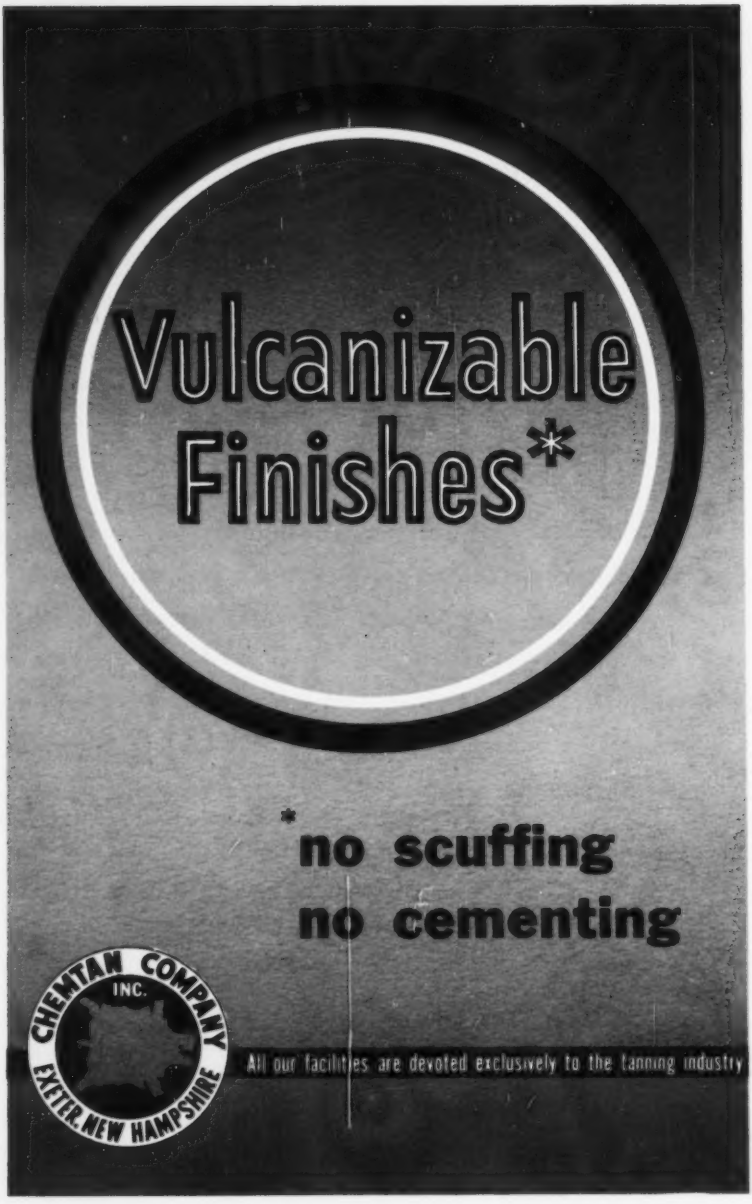
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